

Studies on the Bromination of *cis*- and *trans*-PiperyleneVICTOR L. HEASLEY,^{1,2} GENE E. HEASLEY,³ STEPHEN K. TAYLOR, AND CHARLES L. FRYEDepartment of Chemistry, Pasadena College, Pasadena, California 91104,
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A study of the bromination of dilute (ionic conditions) and concentrated (radical conditions) solutions of *cis*- and *trans*-piperylene, and further investigations on the bromination of isoprene (concentrated solutions) are reported. The following products were formed in varying quantities depending on the conditions, in the bromination of *cis*- and *trans*-piperylene: 3,4-dibromo-1-pentene (*erythro*-1a and *threo*-1b), 4,5-dibromo-2-pentene (*cis*-2a, and *trans*-2b), *cis*-1,4-dibromo-2-pentene (3), and *trans*-1,4-dibromo-2-pentene (4). The principal differences in the bromination of the piperylenes in dilute and concentrated solutions are that, for the former conditions, bromine addition is completely stereoselective to give 1b and 2a from *cis*-piperylene, and 1a and 2b from *trans*-piperylene, whereas addition under the latter conditions is considerably less stereoselective. Detailed comparisons are made of the results of the brominations of butadiene, the piperylenes, and isoprene. Mechanistic interpretations of the results are suggested.

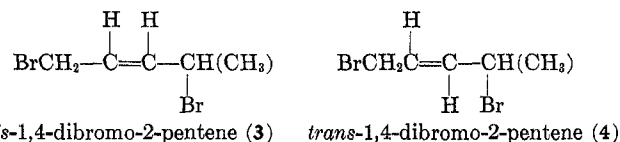
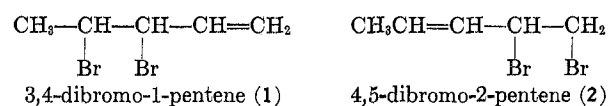
It has recently been shown that the addition of bromine to the 2-butenes is essentially stereospecific,⁴ whereas bromination of certain styrene systems is only 83–88% stereospecific.^{4,5} These data were interpreted as meaning that in the former case symmetrically bridged bromonium ion intermediates are involved which do not allow rotation around the 2,3 bond. The intermediates in the bromination of the styrenes are best described as unsymmetrically bridged bromonium ions, in which the carbonium ion is stabilized by interaction with the phenyl ring. Weak bonding between the bromine atom and the benzylic carbon atom permits rotation around the 1,2 bond and, hence, loss of stereospecificity. We felt that a determination of the stereoselectivity in the addition of bromine to *cis*- and *trans*-piperylene would provide insight into the nature of the intermediates in these reactions, and would allow a comparison to be made between a benzene ring and a vinyl group in terms of their relative abilities to interact with and disperse the charge from a bromonium ion. Loss of stereospecificity would be indicated by addition to the terminal double bond of a piperylene accompanied by isomerization of the 3,4 double bond, or by a nonstereospecific addition to the internal double bond, and would suggest extensive dispersal of charge across the allylic system.

Since a previous study on the bromination of butadiene had shown that addition could occur by either an ionic or radical mechanism depending upon the olefin concentration,^{6,7} we needed to explore this problem with the piperylenes, and decided also to include isoprene since this aspect has not been investigated in a previous study of isoprene bromination.⁸ Judging from results with butadiene, it was anticipated that bromination at 0.02 mol fraction of olefin would proceed entirely by an ionic mechanism and at 0.8 mol fraction by at least in part a radical mechanism.

Comparison of the results from the bromination of the piperylenes and isoprene might help elucidate factors affecting 1,2 and 1,4 addition. We also wished to determine whether the *cis* and *trans* double bonds

would show a significant difference in reactivity as has been observed in the reaction of methanesulfonyl chloride with monoolefins.⁹

The structures of the dibromides which could theoretically be obtained from the bromination of piperylene are structures 1–4. Isomer 1 can exist as either of two



diastereoisomers (1a, *erythro*, and 1b, *threo*) and 2 can exist as either *cis*-2a or *trans*-2b isomers. The dibromides from isoprene have been described previously.⁸

Results and Discussion

The dibromides formed in the bromination of the piperylenes and isoprene under various conditions are summarized in Table I.

The results in Table II show that the stereoselectivity in the addition of bromine to *cis*- and *trans*-piperylene varies with the concentrations of the olefin.

Runs 1 and 6 (Table II) indicate that the bromination under ionic conditions is stereoselective within the limits of the analytical method. Addition to the terminal double bond occurs without isomerization of the internal *cis* or *trans* double bond and addition to the internal double bond (*trans* addition) yields one stereoisomer from the *cis* alkene and another from *trans*. This is in contrast to the bromination in carbon tetrachloride of the β -methylstyrenes where the addition was about 88–83% stereospecific,^{4,5} but is in agreement with the results observed for *cis*- and *trans*-2-butene where at least 99.5% stereoselectivity was observed.⁴ We interpret our results to mean that the intermediates in these diene additions are rather tightly bridged bromonium ions (see structures 5 and 7) without appreciable delocalization of charge. We reject the possibility of the involvement of intermediates with charge delocalization (see structures 6 and 8) on the basis of the following considerations. Delocalization of charge

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(4) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969).(5) R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968).(6) V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34**, 2779 (1969).(7) For similar studies involving chlorination of alkenes, see papers by M. L. Poutsma, e.g., M. L. Poutsma, *ibid.*, **31**, 4167 (1966).(8) V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *ibid.*, **33**, 2342 (1968).(9) W. A. Thaler, *ibid.*, **34**, 871 (1969).

TABLE I
 BROMINATION OF *cis*- AND *trans*-PIPERYLENE AND ISOPRENE, -15°

Run	Diene	Mol fraction of diene	Conditions ^a	Percentage of dibromides			
				I	II	III	IV
1	<i>cis</i> -Piperylene	0.02		13	31		56
2	<i>cis</i> -Piperylene	0.8		3.5	23	0.5	73
3	<i>cis</i> -Piperylene	0.8	Inhibitor	3	23		74
4	<i>cis</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent)	3.5	22.5	1	73
5	<i>cis</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent), light	4.5	26	1.5	68
6	<i>trans</i> -Piperylene	0.02		0.5	35		64.5
7	<i>trans</i> -Piperylene	0.8		1	25	1	73
8	<i>trans</i> -Piperylene	0.8	Inhibitor	Trace	27	0.5	71.5
9	<i>trans</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent)	1	27	Trace	72
10	<i>trans</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent), light	2	27.5	2.5	68
11	Isoprene	0.02		23	2	2	73
12	Isoprene	0.8		10	6.5	9	74.5
13	Isoprene	0.5	C ₆ H ₅ Me (solvent)	13	6.5	6.5	74
14	Isoprene	0.5	C ₆ H ₅ Me (solvent), light	10	7	10	73

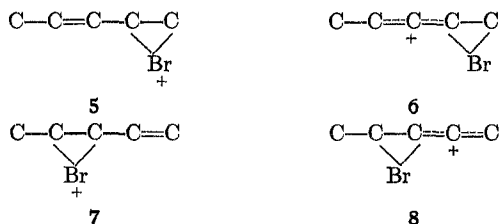
^a The normal conditions are reported in the Experimental Section. Deviations are noted here. ^b I = 1 from piperylene and 3,4-dibromo-3-methyl-1-butene from isoprene, II = 2 from piperylene and 3,4-dibromo-2-methyl-1-butene from isoprene, III = *cis*-1,4-dibromides, IV = *trans*-1,4-dibromides.

 TABLE II
 STEREOSELECTIVITY IN THE BROMINATION OF *cis*- AND *trans*-PIPERYLENE

Run ^a	Diene	Mol fraction of diene	Conditions ^b	Stereoisomers, %			
				1a	1b	2a	2b
1	<i>cis</i> -Piperylene	0.02			100	100	
2	<i>cis</i> -Piperylene	0.8		15	85	73	27
3	<i>cis</i> -Piperylene	0.8	Inhibitor	8	92	90	10
5	<i>cis</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent), light	36	63	41	59
6	<i>trans</i> -Piperylene	0.02		100			100
7	<i>trans</i> -Piperylene	0.8		55	45	2	98
10	<i>trans</i> -Piperylene	0.5	C ₆ H ₅ Et (solvent), light	50	50	2	98

^a The numbers of the runs in this table are identical with those in Table I. ^b See footnote b in Table I.

would result in a weakening of the carbon-bromine bond (see structure 8), rotation around the 3,4 bond would be expected (by analogy to the styrene systems⁵), and loss of stereospecificity would result. In the addition of bromine to the terminal double bond of either piperylene, if intermediates with delocalization of charge are involved (see structure 6), the π bonding between carbon atoms 3 and 4 would be reduced, and isomerization could occur. Isomerization would be particularly favored when the internal double bond has the *cis* con-



figuration. In a previous study we showed that there is little, if any, delocalization of charge in the intermediates involved in the bromination of butadiene in methanol. The results reported in the present study support this earlier investigation.¹⁰

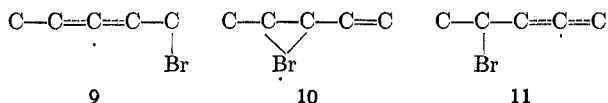
Runs 2 and 7 (Table II) indicate that the addition of bromine to *cis*- and *trans*-piperylene at high mole fraction is considerably less stereoselective than under ionic conditions. Evidence is presented in the Experimental Section to show that this effect is not due to rearrangement of the diene or of the dibromide products. The evidence for a radical mechanism for *cis*- and *trans*-piperylene under these conditions is not so clear as it

was with butadiene. In the case of butadiene a radical mechanism was demonstrated by competitive bromination of ethylbenzene. However, with *cis*- and *trans*-piperylene no bromination of ethylbenzene, *cis*-1,2-dichloroethylene, or trichloroethylene occurred when the mole fraction of the radical scavenger and the dienes was 0.5.¹¹ The failure of these scavengers to compete for bromine under these conditions may be due to the greater reactivity of the piperylenes as compared with butadiene toward bromine atoms, the lower reactivity of the radicals formed in these reactions, or to a smaller radical component. On the basis of the very similar molecular structures of butadiene and the piperylenes, we feel that the latter are probably reacting in part by a radical mechanism at high mole fraction, but that a sufficiently sensitive method for detecting it has not been developed. In support of this assumption, we found that addition of the radical inhibitor, 2,6-di-*t*-butyl-4-methylphenol, to reaction at high concentration of diene resulted in considerable restoration of stereoselectivity (run 3, Table II).

If bromine does add to the piperylenes by a radical mechanism at high mole fraction, and considering the loss of stereospecificity as shown in Table II, the conclusion can be made that the intermediate radical resulting from attack by bromine atom at the terminal double bond must be a highly delocalized radical with sufficient weakening of the internal double bond to per-

(11) Also, bromination of isoprene at high mole fraction in the presence of toluene or *n*-propylbenzene did not lead to benzyl bromide or α -bromopropylbenzene. However, α -bromoethylbenzene and benzyl bromide were formed during the bromination of the piperylenes in ethylbenzene and isoprene in toluene, respectively, at high mole fraction and under sun lamp irradiation.

mit rotation. (See structure 9.) Also, if attack occurs at the internal double bond, a 3-membered, symmetrically bridged radical intermediate (see structure 10) can hardly be involved, since loss of stereospecificity must occur by rotation around the 3,4 bond. The intermediate probably resembles structure 11, with perhaps, a weak bond between the bromine atom and the neighboring allylic radical. Formation of 1 with much less



stereoselectivity from *trans*-piperylene than from *cis*-piperylene may be due to the fact that the attack on the internal double bond of the *trans* isomer occurs mainly *via* a radical pathway, whereas the *cis* isomer has a significant ionic component to its addition.

The greater reactivity of the internal double bond toward ionic addition in *cis*-piperylene compared with *trans*-piperylene seems to be supported by the data in Table I. Runs 1 and 6 (Table I) suggest that the larger amount of internal addition obtained in *cis*-piperylene (13% *vs.* 0.5% for *trans*) is a true reflection of the reactivity of the *cis vs.* the *trans* double bond, since the bromonium ion obtained for each of these would be expected to afford nearly equal opportunity for 1,2 *vs.* 1,4 attack. This relative reactivity of 26:1 is similar to that observed by Thaler in the addition of methanesulfonyl chloride to alkenes, where *cis*-2-butene was found to be 18 times as reactive as *trans*-2-butene.⁹

The results in Table I show that changing the mole fraction of diene from 0.02 to 0.8 affects significantly the proportions of dibromides formed. With butadiene the percentage of 1,4 addition was observed to change from 40% at 0.02 mol fraction to 80% at 0.4 mol fraction.⁶ The piperylenes and isoprene also show similar changes although the percentage of 1,4-addition product is much larger at 0.02 mol fraction for the piperylenes and isoprene than for butadiene.

The data in Table I show that 1,2 addition in isoprene occurs primarily (11:1) at the methyl substituted double bond, but in the piperylenes at the unsubstituted double bond (*cis*, 2.5:1, and *trans*, 70:1). These data may not reflect the ratios of initial bromonium ion formation, since the source of 1,4-addition product is unknown. However, it is of interest to note that the sulfonyl halides, which give no 1,4 addition, yield similar 1,2-addition products with these dienes. Methanesulfonyl chloride adds to piperylene 86% at the unsubstituted bond and to isoprene 57% at the methyl substituted bond.¹²

Of the four dienes which we have studied, only isoprene yields a detectable quantity of *cis*-1,4-dibromide under ionic conditions. Apparently the ratio of *cis*- to *trans*-1,4-addition products formed under ionic conditions does not reflect the ratio of conformers (*cisoid* and *transoid*), since butadiene which has been shown to consist of 4% *cisoid* conformer gives no *cis*-1,4-dibromide.¹³ It has been suggested¹⁴ that the conformer population for *trans*-piperylene should be similar

to butadiene, and again in this case no *cis*-1,4-dibromide was formed. However the appearance of *cis*-1,4-dibromide for butadiene and the piperylenes (and an increase in its amount for isoprene) seems to be characteristic of the free-radical reaction at high mole fraction. The ratio of *cis*-1,4-dibromide to *trans*-1,4-dibromide formed in the bromination of these dienes under radical conditions seems to reflect the ratio of *cisoid* to *transoid* conformers present in the diene. This particularly is true for butadiene, isoprene, and *trans*-piperylene. It is more difficult to explain how the *cis*-1,4-dibromide formed in the bromination of *cis*-piperylene can result from the *cisoid* conformer since this conformer probably does not exist. It is conceivable that a 1,4-bridged bromine radical may be involved in the *cis*-1,4-dibromide formation, since such a ring should open to give the *cis* isomer. However, we have no direct evidence that such an intermediate is formed.

Experimental Section

Materials.—All solvents and reagents were obtained commercially in high purity unless otherwise indicated. Isoprene was Phillips Petroleum polymerization grade. The *cis*- and *trans*-piperylenes were shown by vpc to contain less than 1% of the other isomer.¹⁵ The dienes were distilled immediately prior to use. Infrared spectra were obtained in carbon disulfide; nmr spectra are in carbon tetrachloride.

Bromination.—In the general procedure neat bromine was added dropwise (drop size, *ca.* 3 μ l) at a rate of about 2 drops/min to well-stirred carbon tetrachloride solutions of the dienes. Reactions were done in the dark, under an atmosphere of dry nitrogen, at a temperature of -15° . Reaction volumes were about 0.8 ml for concentrated runs and 30 ml for dilute solution runs, although some brominations were done on a considerably larger scale. Reactions were carried to about 20% of completion. A more gradual and constant method of bromine addition was also employed, in which the bromine was run in from a small capillary beneath the surface of the solution (rate of addition, 0.07–0.2 ml/sec). Results obtained did not differ in a significant way from those obtained by dropwise addition. In reactions in which 2,6-di-*t*-butyl-4-methylphenol was used, it was present at a concentration of about 0.1 mol fraction. Two 100-W sun lamps placed 4 in. from the reaction mixture provided irradiation in illuminated runs. Under all conditions studied, reactions were very rapid and no bromine color was observed to develop in the solutions.

Yields of piperylene dibromides amounting to 85% at 0.02 mol fraction and 75% at 0.8 mol fraction were obtained. In large scale bromination the high boiling residue remaining after removal of the dibromides was about 10% of the calculated dibromide weight.

It was found by vpc that unreacted piperylenes had undergone no detectable rearrangement during the course of bromination.¹⁵ An experiment was also performed to show that the piperylene dibromides did not undergo rearrangement during the bromination reaction. *cis*-Piperylene was brominated at 0.02 mol fraction; the dibromide ratios were determined by vpc. Most of the carbon tetrachloride was removed by suction and the resulting dibromide mixture was dissolved in cyclohexene so that the cyclohexene mole fraction was about 0.8. Bromination of this mixture was then done under the usual conditions. Analysis of the piperylene dibromide mixture after this treatment showed that the proportions of 1, 2, and 4 had not changed from the initial analysis and that 1 and 2 had sustained no loss in stereoisomeric purity.¹⁶

(15) The piperylenes were analyzed on 6 ft \times 0.25 in. columns packed with either silver nitrate–ethylene glycol or silver nitrate–benzyl cyanide on Chromosorb W. Less than 1% of either isomer in over 99% of the other can be readily detected.

(16) These conditions should approximate those of 0.8 mol fraction piperylene bromination. In an experiment in which a mixture of *cis*-piperylene and cyclohexene (both about 0.5 mol fraction) was brominated, the cyclohexene to piperylene dibromide ratio was near unity. The addition to piperylene under these conditions was less stereoselective (40%, 1a, and 35%, 2b) than when piperylene was brominated at 0.8 mol fraction in carbon tetrachloride.

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Procedure for Analysis of Products.—The vpc analyses of the products were accomplished with an Aerograph 90 P-3 chromatograph and an F & M 700 chromatograph. Ratios of 1, 2, 3, and 4 were determined under the following conditions, designated column A: flow rate (He), 300 ml/min; column dimensions, 5 ft \times 0.25 in., stainless steel; temperature, 48°; composition, 2.5% SE-30 on 60–80 mesh DMCS Chromosorb W. The retention times of 1, 2, 3, and 4 are, respectively 2.4, 3.4, 4.0, and 5.7 min. Conditions for separation of 1a from 2b and 2a from 2b, designated column B, are flow rate (He), 70 ml/min; column dimensions, 10 ft \times 0.125 in., stainless steel; temperature, 38°; column composition, 3.5% SE-30 on 80–100 mesh DMCS Chromosorb W. Retention times for 1a, 1b, 2a, and 2b are, respectively, 17.5, 18.5, 26.0, and 27.6 min.

Dibromide mixtures were analyzed immediately after completion of reaction with no intermediate isolation steps. Detectable rearrangement did not occur under the conditions of analysis as shown by the fact that dibromide mixtures which were collected from the chromatograph and reinjected did not show a change in composition.

The percentages of the dibromides are based directly on the peak areas. Chromatography of known mixtures of 1, 2, and 4 gave area ratios which did not differ from the actual weight ratios by an amount greater than the uncertainty of the vpc analysis. The percentages of dibromide mixtures as obtained by column A were reproducible for reactions run under the same conditions to less than \pm (percentage of dibromide \times 0.05) except where a dibromide occurred in very small amounts. In analysis of stereoisomer mixtures with column B, the separation was not as complete. Because of the tailing of 2a, small amounts of 2b (<5%) could have escaped detection. For the same reason, and because 1 is formed to the extent of only 1% in low mole fraction brominations of *trans*-piperylene, small amounts of 1b could have escaped detection. It is estimated that less than 2% of 1a or 2a could have been detected in the presence of the other isomer.

Identification of Products.—Chromatograms (column A) from low mole fraction brominations of *cis*- or *trans*-piperylene showed three peaks (1, 2, and 4) with an additional peak 3, occurring in small amounts in products from bromination at high mole fraction. Vpc (column B) showed that peaks 1 and 2 from low mole fraction runs consisted of single components but peaks 1 and 2 from high mole fraction runs were resolved into two peaks. Identification of these peaks were achieved in part distillation of a bromination product. Piperylene was brominated at ca. 0.1 mol fraction in dichloromethane and the product after removal of the solvent under vacuum was fractionated through a 20-cm Nester–Faust spinning-band column at a pressure of 0.5 mm and pot temperature, 50–70°. Fractions corresponding to vpc peaks 1, 2, and 3 were obtained with the following purities as shown by vpc: 1, >99%; 2, 93% (2% 1 and 5% 4); 4, 95% (5% 2).¹⁷ Chromatograph analysis of these fractions on column B showed that 1 was 96% 1b and 4% 1a, and 2 was 82% 2b and 18% 2a. Unless otherwise stated nmr, ir, and other measurements were made with these fractions.

3,4-Dibromo-1-pentene (1).—The component corresponding to vpc peak 1 was assigned structure 1 on the following basis. In addition to alkene absorption bands at 3100 cm^{-1} and 1640 cm^{-1} , the ir spectrum showed strong absorption bands at 934 and 985 cm^{-1} , the latter two bands being typical of the proposed terminal vinyl structure.¹⁸ The nmr spectrum¹⁹ was distinctly different from that of the other three compounds under consideration, all three of which gave nmr spectra which were very similar in their gross features. In this compound absorptions could be assigned to three separate vinyl hydrogens, and two different methine hydrogens: nmr δ 1.76 (d, 3, CH_3), 4.31 (double quartet, 1, BrCHCH_2), 4.71 (dd, 1, $\text{BrCHCH}=\text{CH}_2$), 5.19 (d, 1, *cis*- $\text{HCH}=\text{CH}$), 5.28 (d, 1, *trans*- $\text{HCH}=\text{CH}$), 5.95 (octet, 1,

$\text{CH}_2=\text{CH}$). The apparent coupling constant between the hydrogens of carbons 3 and 4 was found to be 4.0 Hz. On this basis 1b may be reasonably assigned the *threo* structure, the expected structure resulting from *trans* addition to the *cis* double bond. The most stable conformer of the *threo* dibromide have the hydrogens *gauche* with an expected coupling constant of about 4 Hz, but the most stable *erythro* conformer has the hydrogens *anti* and consequently an expected coupling constant of 9–11 Hz.⁵

4,5-Dibromo-2-pentene (2).—The nmr of peak 2 was consistent with structure 2: nmr δ 1.78 (d, 3, CH_3), 3.64 [1, d, BrC(H)H], 3.75 [1, d, BrC(H)H], 4.65 [double quartet, 1, $\text{BrCH}_2\text{C(H)Br}$], 5.3–6 (m, 2, $\text{CH}=\text{CH}$). The most significant evidence for assignment of structure 2 to vpc peak 2 is that the compounds corresponding to this peak have different structures depending upon whether *cis*- or *trans*-piperylene was brominated at low mole fraction. The ir spectrum of peak 2 collected from vpc of the product of bromination of *trans*-piperylene showed, in addition to absorption bands at 3040 and 1660 cm^{-1} , a strong absorption band at 958 cm^{-1} characteristic of the *trans* double bond. Peak 2 collected from vpc of the product resulting from bromination of *cis*-piperylene showed absorption bands in its ir at 3040 and 1660 cm^{-1} with its most prominent absorption band at 753 cm^{-1} rather than 958. This absorption band would be expected for the *cis*- $\text{CH}=\text{CH}$ group.

***trans*-1,4-Dibromo-2-pentene (4).**—The compound corresponding to vpc peak 4 showed an nmr spectrum consistent with this structure: nmr δ 1.78 (d, 3, CH_3), 3.92 (d, 2, CH_2Br), 4.62 [quintet, 1, HC(Br)CH_2], 5.76 (m, 2, $\text{CH}=\text{CH}$). The ir spectrum showed the characteristic *trans* absorption at 962 cm^{-1} as well as bands at 3010 and 1670 cm^{-1} .

***cis*-1,4-Dibromo-2-pentene (3).**—3, prepared by independent synthesis, was shown to have a retention time identical with that of peak 3. 2-Pentyne-1,4-diol, n^{20}_D 1.4809 (lit.²⁰ n^{17}_D 1.4819), was prepared by the method of Gouge²⁰ and hydrogenated in a Parr apparatus using the Lindlar catalyst to *cis*-2-pentene-1,4-diol, n^{20}_D 1.4706 (lit.²⁰ n^{16}_D 1.4668 by Raney nickel reduction of the alkyne). Treatment of the diol with PBr_3 according to the method of Valette²¹ yielded 3, bp 40–43 (0.4 mm). Vapor phase chromatography showed that this product was contaminated with 10% 2 and 5% 4. The ir spectrum was similar to that of 4 with absorption bands at 3040 and 1670 cm^{-1} and a weak absorption band at 958 cm^{-1} , possibly due to 2 and 4 contamination; the prominent feature was the strong *cis* absorption ($\text{CH}=\text{CH}$) band at 776 cm^{-1} , similar to the *cis*-2a absorption at 753 cm^{-1} . This absorption band is completely lacking in the spectrum of 4. The gross features of the nmr spectrum were similar to those of 4 but splitting patterns for methine and methylene hydrogens were more complex: nmr δ 1.79 (d, 3, CH_3), 4.0 (m, 2, CH_2Br), 4.97 (double quartet, 1, CH_2CHBr), 5.4–6.0 (m, 2, $\text{CH}=\text{CH}$).

Equilibrium of Isomers.—Further proof that the dibromides are interrelated in the manner proposed is shown by the fact that, when isolated samples of each isomer were heated in sealed tubes for several days at 80°, identical mixtures were obtained in every case. This equilibrium mixture was shown by vpc to consist of 1% 1a, 1% 1b, 5% 2a, 27% 2b, 6% 3, and 60% 4.

Registry No.—*cis*-Piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8; 1a, 25296-34-8; 1b, 25356-02-9; 2a, 25356-03-0; 2b, 25296-35-9; 3, 25356-04-1; 4, 25296-22-4.

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(17) Fraction 1 was obtained by brominating *cis*-piperylene; 2 was obtained from a mixture of piperylenes, mainly *trans*.

(18) For a discussion of the positions of absorption bands in the infrared, see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1957.

(19) d = doublet; dd = double doublet; m = multiplet.