Polar Additions to Olefins and Acetylenes. VI. Nonstereospecific Addition of Bromine to 1-Phenylpropene and *trans*-Anethole[1]

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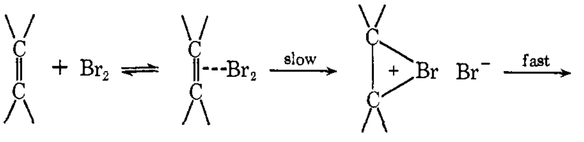
Abstract: It has been established that addition of bromine to *cis*- and *trans*-1-phenylpropenes and to *trans*-anethole in carbon tetrachloride occurs by an electrophilic mechanism and that the additions are nonstereospecific. Bromine addition to *cis*-1-phenylpropene gives a mixture of *erythro*- and *threo*-(1,2-dibromopropyl)benzenes in which the ratio *erythro:threo* is 17:83 and addition to *trans*-1-phenylpropene yields a mixture of the same dibromides in which the *erythro:threo* ratio is 88:12. Bromine addition to *trans*-anethole yields *erythro*- and *threo*-*p*-(1,2-dibromopropyl)anisoles with an *erythro:threo* ratio of 63:37, a value quite close to the equilibrium ratio of 67:33. In all cases it was shown that the starting olefins and the product dibromides are stable to the reaction conditions. Relative rates, determined by the competition method, were found to be: styrene, 1.00; *cis*-1-phenylpropene, 2.1 ± 0.2; *trans*-1-phenylpropene, 4.0 ± 0.5; *trans*-anethole, 1000 ± 200. The results are taken as evidence that the intermediate cation formed in these reactions resembles an open benzylic cation more than a bromonium ion.

It is generally accepted that electrophilic addition of bromine to olefins proceeds *via* an intermediate bromonium ion, as was first postulated by Roberts and Kimball[3] some 30 years ago. While the original suggestion was based mainly upon stereochemical considerations, three lines of evidence now support their conclusion. First, the polar addition of bromine to a variety of olefins has been shown to occur by 1,2-*trans* addition. Examples include bromine addition to maleic and fumaric acids,[4] to *cis*- and *trans*-2-butenes,[5] to cyclohexene,[6] to 4-*t*-butylcyclohexene,[7] and to the cholestenes and related compounds.[8] Similarly, bromine-82 has been shown to add with *trans* stereospecificity to 1-bromocyclohexene.[9] The second line of evidence supporting the bromonium ion mechanism derives from the effect of substituents on the rate of reaction. The bimolecular rate constants, k_2, for addition of bromine to substituted ethylenes in methanolic sodium bromide are correlated by

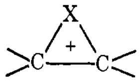
$$\log k_2 = -2.99\sum\sigma^* + 7.61$$

where $\Sigma\sigma^*$ represents the sum of the σ^* values for the four ethylene substituents.[10] This result shows that, in the transition state for bromine addition, positive charge is equally distributed over the two olefinic carbons. Moreover, Dubois and Garnier[11] have recently studied the charge-transfer spectra of bromine–olefin complexes and found that the spectroscopic parameter Γ, which measures the stability of the charge-transfer complex, correlates with log k_2 for bromine addition. This observation has been interpreted as evidence that the over-all mechanism involves rapid reversible formation of a charge-transfer complex followed by rate-limiting ionization to a bromonium ion (eq 1). Thirdly and finally, Olah and Bollinger[12] have recently made nmr measurements on the isobutylene-, trimethylethylene-, and tetramethylethylenebromonium ions and have found that the spectral data support a bridged structure for these cations.



product (1)

The foregoing evidence leaves little doubt that simple ethylene derivatives undergo polar addition of bromine by formation of a bromonium ion intermediate (**1**, X = Br), and analogous stereochemical,[13–15] rate,[14c] and nmr evidence[12] has been obtained which shows that a chloronium ion (**1**, X = Cl) is involved in the chlorination of simple alkenes. On the other hand, the addition of chlorine to acenaphthylene,[16] indene,[17] phenanthrene,[18] *cis*- and *trans*-1-phenylpropenes,[15a] and methyl *trans*-cinnamate,[19] all of which are capable of forming resonance-stabilized benzylic cations, occurs *via* an open ion (**2**, X = Cl) as evidenced by the forma-



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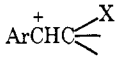

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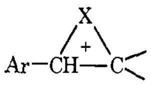

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Table I. Vicinal Coupling Constants in 1,2-Disubstituted 1,2-Dihalides

R_1	R_2	X	Solvent	J_{HH}, Hz Isomer **6**	 Isomer **7**	Ref
CH_3	CH_3	Cl	Neat	6.26	3.28	25
			CS_2	7.39	3.45	25
Ph	CH_3	Cl	CCl_4	8.0	5.7	15a
Ph	$COOCH_3$	Cl	CCl_4	11.0	8.6	19
t-C_4H_9	t-C_4H_9	Cl	CCl_4	5.2	0.8	15b
CH_3	CH_3	Br	Neat	7.87, 7.85	3.03, 3.15	25, 26
			CS_2	8.81	3.11	25
Ph	CH_3	Br	CCl_4	10.2	5.3	*a*
p-$CH_3OC_6H_4$	CH_3	Br	CCl_4	10.0	5.4	*a*

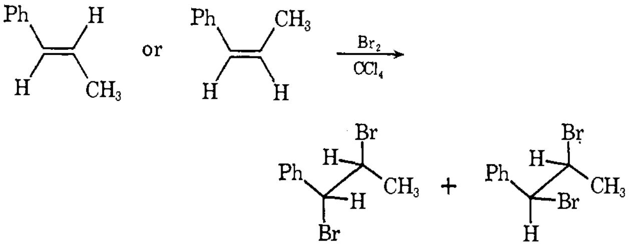
[a] This work.

tion of substantial amounts of *cis*-addition product. Since bromine is a better neighboring group than chlorine, it is not clear whether bromine addition to such conjugated olefins should occur *via* an open benzylic cation (**2**, X = Br) or a bromonium ion (**3**, X = Br). Acenaphthylene and phenanthrene, both of which undergo substantial *cis* addition with chlorine, react with bromine to yield mainly *trans*-addition products.[16,20] These results might suggest that bromine, unlike chlorine, does form a halonium ion intermediate. However, the addition of bromine to *cis*-stilbene has been reported to yield a mixture of *erythro*- and *threo*-1,2-dibromo-1,2-diphenylethanes, and the fraction of *erythro* isomer (*cis* adduct) formed has been found to be larger in polar than in nonpolar solvents.[21,22] Similar results were obtained for addition to *trans*-stilbene.[22] These observations have been interpreted by Buckles[21] and by Heublein[22] as indicating that both bridged and nonbridged intermediates are involved in the reaction. The specific interpretation is somewhat obscured, however, by uncertainties concerning the extent to which the starting stilbene and the product dibromides isomerize under the reaction conditions. It is known that the stilbene dibromides isomerize in the presence of bromine.[23]

The present studies were undertaken in order to obtain further evidence on the structure of the intermediate cation involved in bromine addition to conjugated olefins. We wished to establish the stereochemistry of addition under conditions where both the starting olefins and the product dibromines are stable and where the reaction could be shown to occur by an electrophilic mechanism. We chose 1-phenylpropene as the substrate because results on the stereochemistry of chlorine and of fluorine[24] addition to this olefin, obtained under conditions of known kinetic control, were already available for comparison with the results to be obtained for bromine addition. Including *trans*-anethole (*trans*-*p*-propenylanisole) in the study allowed us to evaluate the effect of a *p*-methoxy group in the phenyl ring on the rate and stereochemistry of addition.

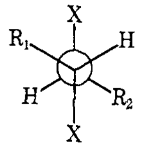
Results

Addition of bromine to either *cis*- or *trans*-1-phenylpropene in carbon tetrachloride yields a mixture of *erythro*- (**4**) and *threo*-(1,2-dibromopropyl)benzene (**5**). Dibromide **4** is the main product of addition to *trans*-1-phenylpropene and dibromide **5** predominates in the addition to *cis*-1-phenylpropene.



4 **5**

The structures of the dibromides were assigned on the basis of their nmr spectra. It has been found that the vicinal H–H coupling in isomeric 1,2-dihalides is larger for isomer **6** (*meso* isomer if $R_1 = R_2$ or *erythro* isomer if $R_1 \neq R_2$) than for isomer **7** (*dl* isomer if $R_1 = R_2$ or *threo* isomer if $R_1 \neq R_2$). This difference in the vicinal coupling constant for the two isomers arises because the coupling varies with the H–C–C–H dihedral angle and because the conformer populations for the two isomers are different.[19,25,26] Representative data are summarized in Table I and provide the basis for assignment of **4** and **5** as the *erythro* and *threo* isomers, respectively.



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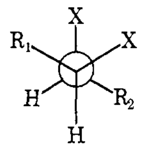

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Preliminary studies of the stereochemistry of bromine addition to 1-phenylpropene were carried out by slowly adding a solution of bromine to a solution of the olefin. Such experiments yielded the same mixture of dibromides, as evidenced by nmr, whether conducted under air or under pure oxygen. Moreover, when such experiments were carried out in the presence of 2,6-di-*t*-butyl-*o*-cresol, a free-radical inhibitor, the product composition remained the same within experimental error. This indicates that the reaction does not involve a free-radical process. The results of quantitative studies in several solvents are summarized in Table II. In these experiments, small amounts of gaseous bromine diluted with oxygen were passed into solutions of the olefin,

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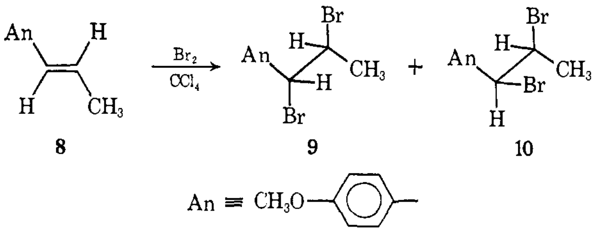
Table II. The Stereochemistry of Bromine Addition to 1-Phenylpropenes[a]

Olefin	Solvent	% conversn followed	Dibromide compn % *erythro*[b]	% *threo*[b]
cis-1-Phenylpropene	CCl_4	22–81	17	83
	$CDCl_3$	45–66	22	78
	CH_2Cl_2	28–100	26	74
trans-1-Phenylpropene	CCl_4	15–100	88	12
	$CDCl_3$	32–100[c]	84	16
trans-Anethole	CCl_4	20–100	63	37

[a] At 2–5°. [b] ±2%. [c] Up to 5% of substitution products were also present in the product.

and the composition of the reaction mixture was determined at varying degrees of conversion by nmr analysis. Examination of the olefinic proton region of the nmr spectra of the reaction mixture after at least 50% conversion revealed that the remaining olefin had retained at least 95% isomeric purity. Since a different product composition is obtained from *cis*- than from *trans*-1-phenylpropene and since the product compositions show no variation with the extent of conversion, it is evident that the products are stable to the reaction conditions. Consistent with this is the fact that when either of the product dibromides was exposed to 0.2 *M* solutions of bromine in carbon tetrachloride, only slow isomerization was observed. Attempts to obtain complete isomerization of the dibromides were thwarted by the occurrence of side reactions.

The stereochemistry of bromine addition to *trans*-anethole (**8**) was also studied. Additions carried out in carbon tetrachloride as solvent yielded a mixture of dibromides **9** and **10**. Dibromide **9** was assigned as *erythro*-*p*-(1,2-dibromopropyl)anisole and dibromide **10** as *threo*-*p*-(1,2-dibromopropyl)anisole from the observed magnitudes of the C_1H–C_2H vicinal coupling constants (Table I). Additions carried out in chloroform as solvent resulted in the formation of significant amounts of substitution products, as evidenced by the formation of hydrogen bromide and by the disappearance of aromatic proton resonance lines in the nmr spectra of the products, and were not studied in detail. Table II includes quantitative data on the stereochemistry of bromine addition to *trans*-anethole in carbon tetrachloride. From the nmr spectra of the partially reacted samples it could be established that the starting olefin does not isomerize during the course of the addition. The product composition does not vary significantly with the extent of reaction which implies either that the products are stable to the reaction conditions or that rapid isomerization to an equilibrium mixture occurs. In order to decide which of these two cases applies, experiments on the stability of **9** and **10** to the reaction conditions were undertaken.



Pure **9** was readily obtained by fractional crystallization of the reaction product mixture. When a solution of **9** in carbon tetrachloride containing about 0.05 *M* bromine was allowed to stand at 25°, a slow isomerization to **10** took place. After 90 min the mixture contained 83% **9**, and a constant composition of 67% **9** was reached after 3000 min. Since lower bromine concentrations and much shorter reaction times are involved in the addition experiments, we conclude from this result that **10** is not formed by secondary isomerization of **9** in the addition of bromine to *trans*-anethole.

Attempts to obtain **10** in pure form were unsuccessful, but mixtures enriched in **10** could be obtained through fractional crystallization of the reaction product and these proved suitable for isomerization studies. When a 1:1 mixture of **9** and **10** was dissolved in carbon tetrachloride containing 0.1 *M* bromine and allowed to stand at 25°, isomerization to a mixture containing 64% of **9** occurred after 5 min and a stable mixture containing 67% of **9** was obtained after 100 min. This result, coupled with the results on the isomerization of **9**, indicates that the equilibrium mixture consists of **9** and **10** in a 2:1 ratio. Since the conditions for the isomerization experiments are more severe than those involved in the addition experiments, these results suggest that **10** does not isomerize to **9** during the addition reaction.

It was definitely shown that **10** does not isomerize to **9** under the conditions for addition by treating a known mixture of **8**, **9**, and **10** in carbon tetrachloride with bromine and examining the composition of the resulting dibromide mixture. The data are summarized in Table III. If isomerization of **9** were accompanying addition, then the final ratio of **9**:**10** in these experiments should be the same (63:37) as found for addition to *trans*-anethole alone. If isomerization does not accompany addition, then the final ratio of **9**:**10** in these experiments will differ from that found for addition to *trans*-anethole and can be calculated from the known initial composition. The results of Table III show that the final compositions are, within experimental error, equal to those expected if no isomerization occurs. From the foregoing experiments we conclude that bromine addition to *trans*-anethole in carbon tetrachloride gives a mixture of dibromides which is very close to the equilibrium mixture but that the dibromides are formed under conditions of kinetic control.

Table III. Test for Isomerization of **9** and **10** under Conditions for Bromine Addition to *trans*-Anethole

Initial composn % 8	% (9 + 10)	9:10	Composition after addition of Br_2 % 8	% (9 + 10)	9:10 Obsd	Calcd[a]
69	31	49:51	0	100	58:42	59:41
54	46	49:51	7	93	54:46	56:44

[a] Assuming no isomerization.

The rates of addition of bromine to the 1-phenylpropenes and to *trans*-anethole were determined in carbon tetrachloride relative to the rate of addition to styrene. Relative rates were determined at 20° by the competition method using nmr for product analysis; details are given in the Experimental Section. The relative rates were found to be: styrene, 1.00; *cis*-1-phenylpropene, 2.1 ± 0.2; *trans*-1-phenylpropene, 4.0 ± 0.5; *trans*-anethole, 1000 ± 200. A direct comparison of *cis*- with *trans*-1-phenylpropene yielded a rate ratio (*cis*:*trans*) of 0.7 ± 0.2.

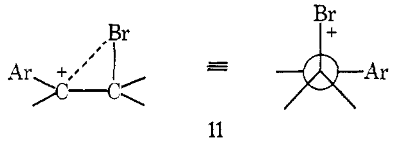
Discussion

The results show that the addition of bromine to *cis*- and *trans*-1-phenylpropenes and to *trans*-anethole is a nonstereospecific process. The lack of stereospecificity cannot be ascribed to prior isomerization of the olefin or to secondary isomerization of the product dibromides, since the olefins as well as the dibromides have been shown to be stable to the reaction conditions. The fact that *trans*-anethole reacts substantially faster than *trans*-1-phenylpropene indicates that the reaction involves an electrophilic mechanism rather than a free radical mechanism. The absence of an effect of free-radical inhibitors on the observed product compositions confirms this view. It is clear then that the stereochemical results must be explained within the framework of the mechanism of electrophilic addition of bromine to olefins.

The results of the relative rate studies indicate that the transition state for addition to 1-phenylpropene has an unsymmetrical structure. Thus, *trans*-anethole reacts about 250 times faster than *trans*-1-phenylpropene which indicates that there is a moderately large amount of positive charge at the benzylic carbon in the transition state for addition to 1-phenylpropene. On the other hand, 1-phenylpropene reacts only two- to fourfold faster than styrene which shows that methyl substitution at the β position of styrene has only a small effect on the rate of reaction and that there must, therefore, be relatively little positive charge at the β carbon in the transition state for addition.[27] The transition state thus resembles a benzylic cation more than a bridged bromonium ion.

Yates and Wright[29] have measured the rates of second-order bromine addition to styrenes bearing electron-withdrawing substituents in acetic acid as solvent and find that they correlate with σ giving $\rho = -2.24$. From the magnitude of ρ they conclude that the transition state for addition has a highly unsymmetrical but nevertheless bridged structure. On the other hand, Dubois and Schwarcz[30] have studied the rates of addition of bromine to styrenes substituted with electron-donating substituents in methanolic sodium bromide and find $\rho = -4.30$ for a correlation with σ^+. The different values of ρ found in these two studies might be attributed to the different solvents involved, but Dubois and coworkers[31] have found that the relative rates of addition to various alkyl-substituted ethylenes vary little with solvent. An alternative explanation is that the transition-state structure is changing with the nature of the substituent such that styrenes bearing electron-donating substituents form essentially unbridged transition states while styrenes substituted with electron-withdrawing substituents form substantially bridged transition states. Styrene, and presumably 1-phenylpropene as well, would then be viewed as forming only a weakly bridged transition state.

If the transition state for addition to 1-phenylpropene resembles a weakly bridged species such as **11**, then it is reasonable to conclude that the initially formed intermediate also resembles **11**. One might then assume that the observed preferential, but not stereospecific, *trans* addition observed with 1-phenylpropene is a consequence of the weak bridging present in **11**. However, collapse of even a weakly bridged intermediate like **11** to *cis* addition product should be quite unfavorable since it would require that the product be formed in a conformation such as **12** in which the two C–Br bonds are eclipsed. For this reason, we believe that the initially formed ion must undergo a rotation about the C_1–C_2 bond before collapse to a *cis* adduct can take place. The preferential *trans* addition of bromine to *cis*- and *trans*-1-phenylpropene can then be viewed as the consequence of a weak bridging interaction restricting rotation in the initially formed intermediate. This description of the mechanism is illustrated for addition to *trans*-1-phenylpropene in Scheme I. In the intermediate formed from *trans*-anethole, such bridging is substantially eliminated by delocalization of the positive charge onto the methoxyl group; rotation about the C_1–C_2 bond is relatively more facile and collapse to product is dictated more by product stability than by bridging phenomena. In any case, it is clear that the driving force for bridging of bromine from a secondary alkyl to a secondary benzylic carbonium ion center is inadequate to control the stereochemistry of bromine addition to 1-phenylpropene.



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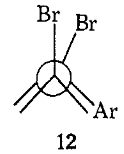

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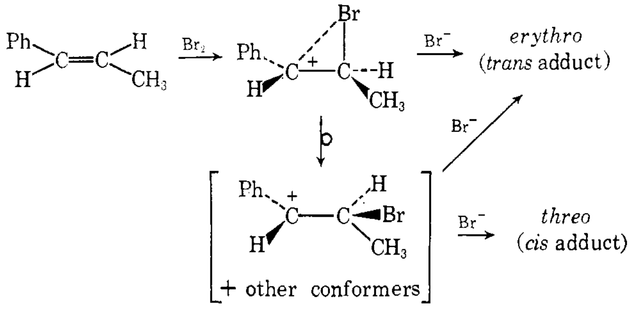
Scheme I



The foregoing conclusions lend support to the idea that the previously observed nonstereospecific additions of bromine to *cis*- and *trans*-stilbenes are, at least in part, the result of formation of an open or only partly bridged cation as the product-determining intermediate.[21,22] The fact that acenaphthylene[16] and phenanthrene[20] yield *trans*-addition products with bromine cannot be taken as strong evidence for a bromonium ion intermediate since, if an open cation were formed in these reactions, collapse to *trans* adduct could be favored

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(27) This can be contrasted with the relative rates of bromine addition to propylene ($k_{rel} = 1.00$), *cis*-2-butene ($k_{rel} = 43$), *trans*-2-butene ($k_{rel} = 28$), and isobutylene ($k_{rel} = 89$) in methanolic sodium bromide;[28] here methyl substitution produces a substantial increase in rate and the magnitude of the increase is largely independent of the position of substitution. This indicates that substantial positive charge is present at both olefinic carbons in the transition state for addition to propylene.

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Table IV. The Stereochemistry of Electrophilic Additions to 1-Phenylpropene

Reagent	Conditions	Olefin	% *cis* addn	Ref
DBr	CH_2Cl_2, 0°	1-Phenylpropene	88[a,b]	*c*
F_2	CCl_3F, −126°	1-Phenylpropene	78,[a] 73[b]	24
Cl_2	CCl_4, 0°	1-Phenylpropene	62,[a] 46[b]	15a
Br_2	CCl_4, 2–5°	1-Phenylpropene	17,[a] 12[b]	This work
INCO	Et_2O	β-Deuteriostyrene	0[d]	32
ArSCl[e]	CCl_4, 25°	1-Phenylpropene	0[d]	*f*

[a] From *cis* olefin. [b] From *trans* olefin. [c] M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963). [d] Nmr analysis showed no detectable *cis*-addition product. [e] Ar = 2,4-di-$NO_2C_6H_3$ or 4-ClC_6H_4. [f] Private communication from Professor G. H. Schmid, University of Toronto.

because of the greater stability of 1,2-*trans* adducts than of 1,2-*cis* adducts in cyclic systems.

One of the reasons for undertaking the present study was to obtain data on the stereochemistry of bromine addition to 1-phenylpropene which could be compared with the results of other electrophilic additions to this type of olefin. Stereochemical results for addition of various electrophilic reagents to 1-phenylpropene are summarized in Table IV. Data on the electrophilic addition of iodine to 1-phenylpropene are not available, but Hassner and Heathcock[32] have shown that iodine isocyanate adds stereospecifically *trans* to β-deuteriostyrene and this indicates that the addition of electrophilic iodine reagents to 1-phenylpropene is also likely to occur entirely *trans*. The observation that iodine chloride adds *trans* to *trans*-stilbene[33] and the isolation in good yield of *trans* adducts from the addition of iodine azide to *cis*- and *trans*-stilbenes[34] provide further support of this conclusion.

The results of Table IV show that the stereochemistry of electrophilic addition to 1-phenylpropene changes with the nature of the electrophilic reagent. The reason for this change is clear. Since hydrogen, fluorine, and chlorine are all relatively poor neighboring group atoms, electrophilic additions to 1-phenylpropene involving deuterium bromide, fluorine, and chlorine proceed *via* open carbonium ions (**2**) and are nonstereospecific. The tendency toward *cis* addition observed with these reagents is the logical consequence of ion-pairing phenomena in nonpolar solvents. On the other hand, iodine and ArS– are very good neighboring groups so that the addition of INCO or ArSCl to 1-phenylpropene can be reasonably expected to proceed *via* a bridged intermediate **3** and to occur with *trans* stereospecificity. Bromine, which is a better bridging atom than chlorine but poorer than iodine, represents an intermediate case. Thus, the present finding that the addition of bromine to 1-phenylpropene occurs preferentially, but not stereospecifically, *trans* is sensibly interpreted as indicating that the initially formed intermediate has an only partially bridged structure as represented by **11.**

Experimental Section

All nmr measurements were carried out on a Varian HR-60 spectrometer. Samples were measured as 20% w/v solutions in carbon tetrachloride containing TMS as internal standard. Spectra were calibrated by the side-band technique and chemical shifts are reported in parts per million (ppm) downfield from TMS. The purity of starting materials was checked on a Varian Aerograph Series 1200 chromatograph using a 160 ft × 0.01 in. column coated with XF-1150.

Materials. *trans*-1-Phenylpropene (Columbia Organic Chemicals) was purified by fractionation on a spinning-band column after which glpc analysis indicated that it was at least 98% pure. *cis*-1-Phenylpropene was the same as that described previously.[15a] *trans*-Anethole, mp 21° (Matheson Coleman and Bell), found by both glpc and nmr to contain no detectable impurities, was used without further purification. Bromine was reagent grade and styrene (Matheson Coleman and Bell) was freshly distilled before use. Carbon tetrachloride and deuteriochloroform were spectroquality solvent and methylene chloride was chromatoquality reagent grade.

Bromine Addition to 1-Phenylpropene. Initial experiments were carried out by adding a 2 *M* solution (5 ml) of bromine to a 2 *M* solution (5 ml) of the olefin over 10 min with stirring. Samples were withdrawn at intervals during the addition, the solvent evaporated, and the residue analyzed by nmr. Experiments carried out under air, under oxygen, and in the presence of 2,6-di-*t*-butyl-*p*-cresol (50–200 mg) gave essentially identical results with those reported in Table II. The experiments of Table II were carried out as follows: oxygen was passed first through a sulfuric acid wash bottle, then through a calibrated trap containing the required amount of bromine, and finally through a 1 *M* solution of the 1-phenylpropene. The reaction vessel was immersed in an ice bath and protected from light during the addition. Experiments in carbon tetrachloride and deuteriochloroform were carried out in an nmr tube, and the progress of the reaction was followed by nmr. Additions in methylene chloride were performed in a three-necked flask; samples were withdrawn at intervals and concentrated by fractionation through a Vigreux column. After addition of carbon tetrachloride to the residue, the last traces of methylene chloride were distilled off and the sample was analyzed by nmr.

The nmr spectra of *erythro*- and *threo*-(1,2-dibromopropyl)benzenes were obtained from a comparison of the nmr spectrum of a completely reacted sample of *cis*-1-phenylpropene with that from a completely reacted sample of *trans*-1-phenylpropene; nmr spectral data for the dibromides are given in Table V. The extent of reaction was calculated both from the observed ratio of olefinic to C_1H dibromide protons and from the ratio of olefinic to C_2CH_3 dibromide protons in the nmr spectrum of the reaction mixture. The ratio of *erythro*- to *threo*-dibromide was determined from the ratio of the dibromide C_2CH_3 peak areas and also from the ratio of the dibromide C_1H peak areas, the two ratios showing good agreement. Since *cis*- and *trans*-1-phenylpropenes exhibit distinctive nmr spectra in the olefinic region, the nmr analysis also established that less than 5% interconversion of the olefins accompanied the addition of bromine.

In the addition of bromine to *trans*-1-phenylpropene in deuteriochloroform, the formation of small amounts of hydrogen bromide was detected and the nmr spectrum of the reaction product showed peaks in the olefinic region which could not be ascribed to either *cis*- or *trans*-1-phenylpropene. It is assumed that these arise from the formation of a small amount (~5%) of 2-bromo-1-phenylpropene.

Bromine Addition to *trans*-Anethole. In a preparative experiment, 16 g (0.1 mol) of bromine was added over 1 hr to a stirred solution of 14.8 g (0.1 mol) of *trans*-anethole in 100 ml of carbon tetrachloride at −2°. After completion of the addition, the reaction mixture was washed with aqueous sodium thiosulfate and the carbon tetrachloride evaporated. A fraction of the residue was recrystallized from ether to yield pure *erythro*-*p*-(1,2-dibromopropyl)anisole (**6**), mp 66°. The nmr spectral data for **6** are given in Table V. Repeated fractional crystallization of the crude dibromide mixture from acetone yielded in the mother liquor a mixture of *erythro*- and *threo*-*p*-(1,2-dibromopropyl)anisoles containing 51%

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(33) G. Heublein, *Z. Chem.*, **6**, 186 (1966).

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Table V. Nmr Spectral Data

Isomer	Protons	δ, ppm[a]	Multiplicity	J, Hz[b]	Rel area
		$PhC_1HBrC_2HBrCH_3$			
erythro	Ph	7.25	Broad singlet	. . .	5
	C_1H	4.96	Doublet	10.2	1
	C_2H	4.49	Doublet of quartets	10.3 6.2	1
	CH_3	2.00	Doublet	6.1	3
threo	Ph	7.23	Broad singlet	. . .	5
	C_1H	5.17	Doublet	5.3	1
	C_2H	4.51	Doublet of quartets	5.4 6.6	
	CH_3	1.67	Doublet	6.6	3
		p-CH_3O–C_6H_4–$C_1HBrC_2HBrCH_3$			
erythro	ArH	6.7–7.4	Approx AB multiplet	9	4
	C_1H	4.99	Doublet	10.0	1
	C_2H	4.52	Doublet of quartets	10.1 6.3	1
	CH_3O	3.71	Singlet	. . .	3
	CH_3	2.00	Doublet	6.1	3
threo	ArH	6.6–7.4	Approx AB multiplet	9	4
	C_1H	5.18	Doublet	5.4	1
	C_2H	4.52	Complex	. . .	1
	CH_3O	3.71	Singlet	. . .	3
	CH_3	1.66	Doublet	6.6	3

[a] ±0.02 ppm. [b] ±0.1 Hz.

of the *threo* isomer **7**. The nmr spectral data for **7** (Table III) were derived by comparison of the nmr spectrum of this mixture with that of pure **6**.

Quantitative studies were carried out in carbon tetrachloride in the same manner as described above for additions to 1-phenylpropene, and the reaction was followed in an analogous manner from nmr measurements. During the course of the additions, the olefinic proton resonance peaks of *trans*-anethole decrease in intensity but no new peaks appeared in the olefinic region. Since *cis*-anethole would exhibit a different resonance pattern in this region, this result indicates that *trans*-anethole does not isomerize to *cis*-anethole under the reaction conditions.

Isomerization Experiments. The desired amount of bromine was added to a 1 M solution of the dibromide in carbon tetrachloride. Experiments were carried out in an nmr tube and the progress of the isomerization followed directly by nmr. The experiments of Table III were performed in the same fashion as the bromine addition experiments described above.

Relative Rate Determinations. Rates were determined relative to styrene by the competition method and relative rates were calculated from the expression

$$k_P/k_S = \log([P]_o/[P]_x)/\log([S]_o/[S]_x)$$

where $[P]_o$ and $[S]_o$ are the respective concentrations of 1-phenylpropene (or anethole) and styrene before addition of bromine and $[P]_x$ and $[S]_x$ are the corresponding concentrations after addition of a limiting amount of bromine. The ratio $[P]_o/[P]_x$ was determined from the ratios of the C_2CH_3 peak areas in the nmr spectrum of the reaction product mixture. The ratio $[S]_o/[S]_x$ was determined indirectly from the ratio of the CH_2Br peak area, A_{CH_2Br}, of styrene dibromide to that of the sum of the methyl (methoxyl in the case of *trans*-anethole) peak areas, A_{CH_3}, and the known value of $[S]_o/[P]_o$ according to the expression

$$\frac{[S]_o}{[S]_x} = \left[1 - \frac{3A_{CH_2Br}[P]_o}{2A_{CH_3}[S]_o}\right]^{-1}$$

The experiments were carried out at 20 ± 2° with 1.0 M solutions of olefin in carbon tetrachloride. The rate studies with 1-phenylpropene were conducted in the same fashion as the experiments reported in Table II. This procedure proved unsatisfactory for *trans*-anethole, however, since reaction occurred more rapidly than mixing of the solution in the nmr tube. Competition experiments between styrene and *trans*-anethole were carried out by stirring a 1.0 M carbon tetrachloride solution of the olefin mixture in a closed reaction flask and introducing the bromine in a specially designed open container above the surface of the solution. In this way the bromine slowly diffused into the solution at low concentration and allowed thorough mixing before reaction took place. That this was so was evident from the accumulation and slow disappearance of bromine color in the solution. After complete reaction of the bromine, the solvent was evaporated and the residue analyzed by nmr. The results of the competition experiments are given in Table VI.

Table VI. Results of Relative Rate Studies

Olefin	$[S]_o/[P]_o$	$[P]_o/[P]_x$	$[S]_o/[S]_x$	k_P/k_S
cis-1-Phenylpropene	9.6	1.3_2	1.1_4	$2._1$
	9.6	3.8_5	1.9_5	$2._8$
	3.3	1.3_5	1.1_8	$1._8$
	3.3	1.9_8	1.3_5	$2._3$
trans-1-Phenylpropene	8.4	3.4	1.3	$4._6$
	5.8	2.8	1.3_3	$3._5$
trans-Anethole	50	8.7	1.002	1040
	67	6.2	1.002_3	880
	100	7.3	1.002	960

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