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Electrophilic Addition to Olefins. III. The Stereochemistry of Addition of Deuterium Bromide to 1-Phenylpropene[1]

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This study was undertaken in order to determine the stereochemistry of the polar addition of hydrogen bromide to an acyclic olefin. It was found that both *cis*- and *trans*-1-phenylpropene add deuterium bromide in methylene chloride at 0° in the presence of 2,6-di-*tert*-butylphenol to give 1-bromo-1-phenylpropane-2-d_1, the polar addition product. With each of the isomeric olefins 88 ± 2% *cis*-addition was found. The results are interpreted in terms of a mechanism, involving ion pair intermediates, proposed earlier for addition of hydrogen halides to olefins.

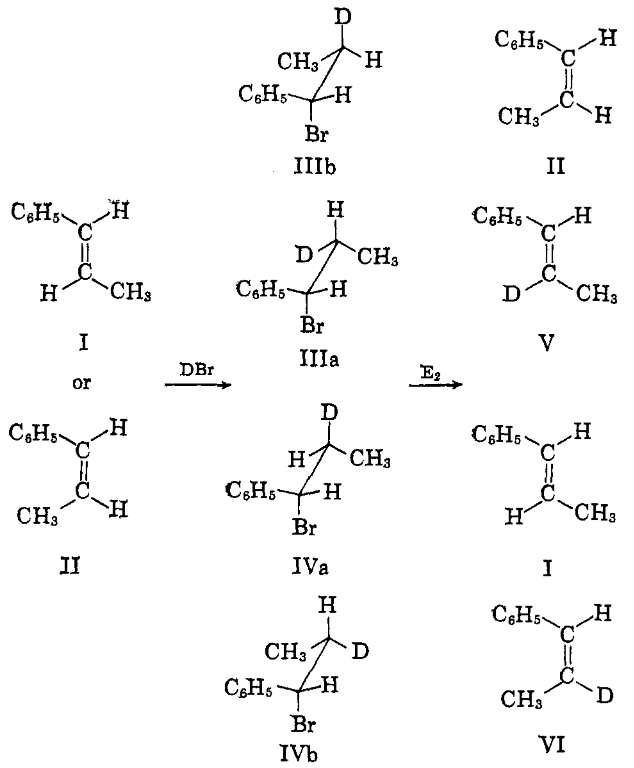
In the previous papers of this series we reported that acenaphthylene[3] and indene[4] react with deuterium halides giving predominant, but not complete, *cis*-addition *via* a polar reaction mechanism. These results contrasted sharply with the earlier findings of Hammond and co-workers where it was shown that both 1,2-dimethylcyclohexene with hydrogen bromide[5] and 1,2-dimethylcyclopentene with hydrogen chloride[6] give almost exclusive *trans*-addition. These very different stereochemical findings indicated that the course of the reaction can be largely determined by the structure of the reacting olefin. It was possible to rationalize both sets of observations in terms of a mechanism involving carbonium ion pairs,[4] but it was evident that additional studies of the stereochemistry of addition as a function of olefin structure would be necessary if the factors influencing the reaction were to be fully understood.

Acenaphthylene and indene were chosen for the initial studies because the rigid rings in these molecules simplified the interpretation of the results with regard to steric effects. All of the studies thus far have been with cyclic olefins, and we felt that an acyclic system should be examined. We were interested in learning whether each member of a *cis* and *trans* isomeric olefin pair would exhibit the same stereochemistry of addition. To test this, *cis*- (I) and *trans*-1-phenylpropene (II) were chosen for study, their structures being very similar to that of indene but differing in that the double bond is not part of a ring system.

Results

It was expected that resonance stabilization by the phenyl group would strongly favor polar addition over free-radical addition with the 1-phenylpropenes. However, it was found that, without special precautions, addition of hydrogen bromide to *trans*-1-phenylpropene in methylene chloride gave 10–20% of 2-bromo-1-phenylpropane, the free-radical addition product. When the reaction was carried out in the dark with added 2,6-di-*tert*-butylphenol as inhibitor, 1-bromo-1-phenylpropane, the polar addition product, was the sole product. In pentane under strong irradiation with ultraviolet light, the addition gave exclusively free-radical addition product. Thus it was possible to obtain either mode of addition by carefully selecting the reaction conditions.

The stereochemistry of the addition was determined by adding deuterium bromide to 1-phenylpropene. Two products, III and IV, were possible depending on whether addition was *cis* or *trans*. The addition products were treated with base under conditions leading to a bimolecular elimination. The elimination could give deuterated or undeuterated *cis*- and *trans*-1-phenylpropenes. Since the planar arrangement of the atoms Br–C_1–C_2–H(D) favoring *trans* elimination[7] is readily obtained with these bromides, it seems safe to assume that the elimination is a stereospecific *trans* process. Thus, *cis*-addition to *trans*-1-phenylpropene followed by elimination gives *cis*-1-phenylpropene (II) and *trans*-1-phenylpropene-2-d_1 (V). *trans*-Addition followed by elimination gives I and VI. Analysis of the products of elimination fixes the stereochemistry of addition. An analogous argument holds for addition to *cis*-1-phenylpropene.



The results for additions carried out with the *cis*- and *trans*-1-phenylpropenes are given in Table I. In all cases it was established by n.m.r. that 1-bromo-1-phenylpropane-2-d_1 was the sole product of addition, and that the addition product was free of unreacted olefin. Also, it could be determined from the n.m.r. spectrum of the deuteriobromide that contamination by hydrobromide did not exceed 3%. Deuterium content in the *trans*-1-phenylpropene obtained on elimination was estimated by mass spectral analysis. The *cis*-olefin present in the elimination product was determined by v.p.c. analysis.

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[1] This work has been supported by a grant from the National Science Foundation and was presented in part at the 144th National Meeting of the American Chemical Society at Los Angeles, Calif., April, 1963.

[2] National Science Foundation Predoctoral Fellow.

[3] M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245 (1963).

[4] M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2248 (1963).

[5] G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).

[6] G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 467.

TABLE I

STEREOCHEMISTRY OF ADDITION OF DEUTERIUM BROMIDE TO 1-PHENYLPROPENE IN METHYLENE CHLORIDE AT 0°

Expt.	Olefin	Elimination products, %			% *cis*-adduct formed
		II + VI	I	V	
1	*trans*	1	15	84	86.5
2	*cis*	5	76.5	18.5	81
3	*trans*	2	12	86	88.5
4	*cis*	6	76	18	81.5

Qualitatively the results show that addition is predominantly *cis* as indicated by the large amount of deuterated *trans*-olefin obtained from the addition–elimination with *trans*-1-phenylpropene (experiments 1 and 3) and the large amount of undeuterated *trans*-olefin obtained for the addition–elimination with the *cis* isomer (experiments 2 and 4). The deuterium content of the *cis*-olefin obtained from the elimination was not determined but is probably near 100% as can be seen from the following argument: bimolecular elimination reactions involve large primary isotope effects ($k_H/k_D = 3$–8).[8] The rate of elimination of conformer IVb should, therefore, be at least three times faster than that of IIIb and that of IIIa at least three times faster than that of IVb. Since the populations of the conformers a and b will be essentially identical in isomer III as in IV, the ratio of *trans*- to *cis*-olefin obtained on elimination will be at least nine times greater for III than for IV. No detectable *cis*-olefin was obtained in an experiment where 1-bromo-1-phenylpropane was eliminated, and only 5–6% was found in experiments 2 and 4 where adduct IV must comprise a large fraction of the bromide mixture. It follows that the ratio of *trans*- to *cis*-olefins obtained in elimination of adduct III must be near or greater than 100, and that the *cis*-olefin found in these experiments is derived almost entirely from adduct IV.

Assuming that all of the *cis*-olefin arises from adduct IV and correcting for the 3% of hydrobromide present in the addition product, the amount of *cis*-addition product formed in the reaction can be determined. The values are given in the last column of Table I. These values need not reflect the actual stereochemistry of the addition, for isomerization of the reacting olefin or the addition product under the conditions of the reaction might complicate the analysis. The latter possibility was readily ruled out by recycling a sample of the deuteriobromide of known analysis (85.0% deuterated *trans*-olefin obtained on elimination) through the reaction procedure. Isolation, elimination, and analysis (85.1% of deuterated *trans*-olefin) showed that isomerization did not occur.

Isomerization of the reactant olefin was evaluated in experiments stopped prior to completion. The unreacted olefin was analyzed by v.p.c. or n.m.r. The results are given in Table II. Isomerization of *trans*-1-phenylpropene during the course of the reaction is only of the order of 1%, but that of *cis*-1-phenylpropene was considerably larger. About 5% of the bromide derived from addition to the *cis*-olefin is actually formed by addition to *trans*-olefin produced by isomerization. This assumes that neither olefin adds hydrogen bromide appreciably faster than the other. This was checked in a competition experiment where it was found that the *cis*-olefin reacts about 18% faster than the *trans*-olefin.

A check was also made to ensure that deuterium was not being incorporated into the olefin prior to product formation. The bromide in mixtures obtained from reactions stopped short of completion was converted to a water-soluble pyridinium salt by treatment with pyridine and was removed by extraction with water. The remaining unreacted olefin was purified by v.p.c. and its mass spectrum determined. The spectrum obtained from the olefin recovered from addition to *cis*-1-phenylpropene was identical with that of authentic undeuterated olefin showing that no deuterium had been incorporated. Experiments with *trans*-1-phenylpropene showed only a small amount (0.6%) of deuterium in the unreacted olefin.

TABLE II

ISOMERIZATION OF 1-PHENYLPROPENE

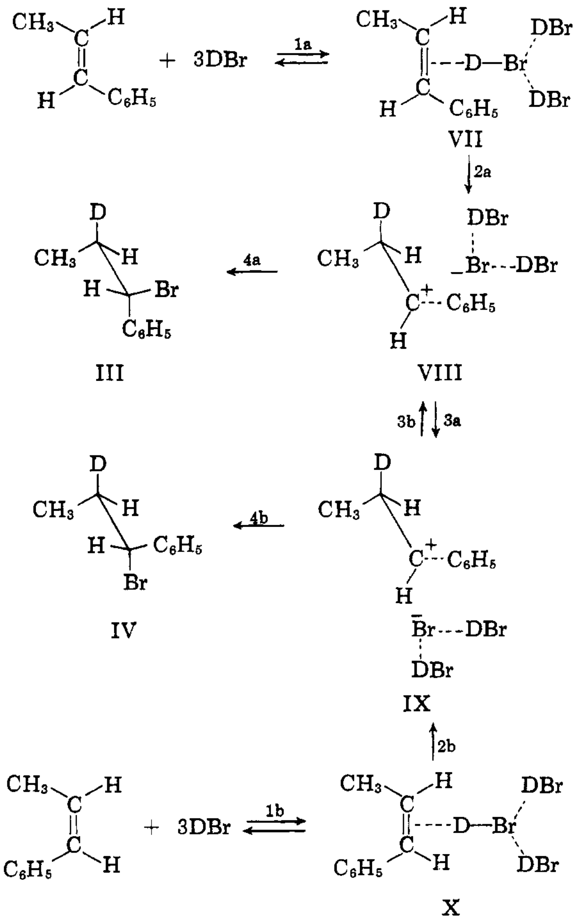
Expt.	Olefin	Reaction,[a] %	Isomerization, %
5	*trans*	14	0.5[b]
6	*trans*	66	1.5 ± 0.5[b]
7	*cis*	12	3 ± 1[a]
8	*cis*	48	5 ± 1[a]
9	*cis*	67	10 ± 2[a]

[a] Determined by n.m.r. [b] Determined by v.p.c.

Correcting for olefin isomerization, the stereochemistry of addition of deuterium bromide in methylene chloride at 0° was found to be 87–89% *cis*-addition to *trans*-1-phenylpropene and 86–90% *cis*-addition to *cis*-1-phenylpropene. Thus the stereochemistry of addition is the same for the two isomeric olefins and is very nearly the same as that found for acenaphthylene (85% *cis*-addition at 0°)[3] and indene (81% *cis*-addition at −78°)[4] in the same solvent.

Discussion

The results reported here for addition to the 1-phenylpropenes can be understood in terms of the mechanism proposed earlier for polar addition of hydrogen halides.[4] This mechanism, as applied to 1-phenylpropene, is illustrated below. In the addi-



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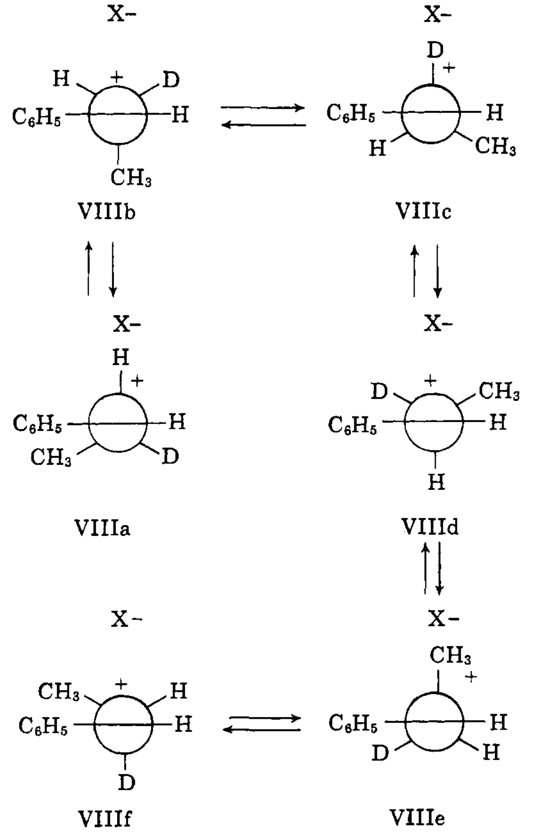
[8] W. H. Saunders and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 139 (1960).

tion to *trans*-1-phenylpropene, an initial equilibrium (step 1a) forms a deuterium halide–olefin complex (VII). Step 2a is rate determining and leads to the ion pair VIII in which the halide ion is associated on the same side of the original olefin plane from which deuteron added. Collapse of VIII (Step 4a) gives the *cis*-addition product III. Alternatively, VIII may rearrange (step 3a) to the ion pair IX in which the halide ion is now on the opposite face of the C_6H_5–C_1–H plane; collapse of this ion pair (step 4b) leads to *trans*-addition product IV. The predominant *cis*-addition observed here is explained if reaction *via* step 4a is about nine times faster than rearrangement *via* step 3a.

In the ion pairs VIII and IX rotation about the C_1–C_2 bond is possible, and six different rotational conformers exist for each ion pair. It seems probable that equilibration between the various conformers occurs faster than collapse to form product or rearrangement to the other isomeric ion pair. Neglecting interaction with the negative ion in the ion pair, the barriers separating rotational forms involve eclipsing of only one pair of bonds, one of which involves an sp^2 hybridized carbon atom, and the barrier is thus expected to be small. A possible exception is the case where the C_1–C_6H_5 and C_2–CH_3 bonds are involved, but all of the rotational conformers are obtainable without crossing the barrier involving eclipsing of these two bulky groups. This is illustrated below for ion pair VIII.



In the addition to *trans*-1-phenylpropene, the ion pair VIII is probably initially formed in conformation VIIIc, but it seems unlikely that collapse occurs directly from this form, since it would lead to a product in which all bonds are eclipsed. Rather, collapse probably occurs from a conformer like VIIIb or VIIId where collapse gives bromide in a staggered conformation. Of course, collapse from any of the conformations VIIIa–f gives the same bromide, and only a rearrangement resulting in transfer of the halide ion to the opposite side of the C_6H_5–C_1–H plane can change the stereochemistry of addition.

If rotation is faster than collapse or rearrangement, then addition to both *cis*- and *trans*-1-phenylpropene can be represented in the same mechanistic scheme as is shown above. The ion pair formed initially from *cis*-1-phenylpropene (step 2b) is identical with the ion pair formed from *trans*-1-phenylpropene by rearrangement of the initially formed ion pair (step 3a). Since the ion pairs VIII and IX are then identical except for interchange of H and D at position C_2, their reactions will have the same rates; thus, the rate of step 4a is equal to that of step 4b and that of step 3a equal to that of step 3b. It follows that *cis*- and *trans*-1-phenylpropene should exhibit the same stereochemistry of addition, as is found.

In this discussion it has been assumed that the reaction is third order with respect to hydrogen bromide. This is consistent with the kinetics of hydrogen bromide addition in nonpolar solvents reported by Mayo and Savoy.[9] In more polar solvents second-order dependence on hydrogen halide is usually found. This change in kinetic order presumably occurs because one molecule of hydrogen halide is replaced by a molecule of solvent in the transition state. Recently Pocker, Naso, and Tocchi[10] reported results of a study of hydrogen chloride addition to styrene in nitromethane. They found the rate to be first order in olefin and second order in hydrogen halide, and showed that, with deuterium chloride, addition was faster than incorporation of deuterium into styrene. This is consistent with the results and interpretation given here.

Experimental

Materials.—1-Phenylpropene (about 80% *trans* isomer) was purchased from Columbia Chemicals and purified by fractional distillation at 80 mm. through a Podbielniak 8 mm. × 24 in. tantalum Heligrid column. Fractions were collected and analyzed by v.p.c. A center cut, b.p. 105°, was collected which analyzed as 99.8% pure *trans*-1-phenylpropene. *cis*-1-Phenylpropene was prepared from phenylacetylene (Columbia Chemicals) as described below. The preparation of deuterium bromide and the other materials used have been described previously.[3]

1-Phenylpropyne.—The procedure used to prepare 1-phenylpropyne was essentially that of Campbell and O'Conner.[11] A 2-l. reaction flask equipped with a stirrer, dropping funnel, condenser, and drying tube was flame dried. After cooling, 300 ml. of 3 *M* methylmagnesium bromide in ether was added and stirring begun. Phenylacetylene (102 g.) was added over 1 hr. The reaction mixture was allowed to stand 24 hr. and then refluxed for 1.5 hr. After cooling, 275 g. of dimethyl sulfate in an equal volume of dry ether was added over 3.5 hr., the rate being adjusted to maintain a slow reflux. After half of the addition was complete, separation of solid made stirring difficult, and 350 ml. of dry ether was added to facilitate stirring. After completion of the addition, stirring was continued for 4 hr. at room temperature and 12 hr. at reflux. At the end of this period, 250 ml. of ether was distilled from the reaction mixture and cold dilute hydrochloric acid added until all solid had dissolved. The ether layer was separated, washed with water, washed with 20% aqueous sodium hydroxide, and again with water. The ether fraction was dried over calcium chloride. After filtration, the solvent was removed on a rotary evaporator and the residue distilled at 15 mm. giving 88 g. of crude product, b.p. 69–75°. This was fractionated at 48 mm. through a Podbielniak 8 mm. × 24 in. tantalum Heligrid column, and fractions collected and analyzed by v.p.c. A total of 64.5 g. of 1-phenylpropyne, b.p. 101–102°, was obtained as well as 7 g. of unreacted phenylacetylene. The yield of product (99% pure by v.p.c.) was 60% based on unrecovered phenylacetylene.

***cis*-1-Phenylpropene.**—1-Phenylpropyne (64 g.) in 230 ml. of absolute ethanol with 2 g. of 10% palladium-on-charcoal was placed in a Parr hydrogenation apparatus and hydrogenated at 40 lb. pressure. The theoretical amount of hydrogen was absorbed in 65 min. After filtration, the solution was dumped into 10% aqueous sodium chloride and the organic layer separated.

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[9] F. R. Mayo and M. G. Savoy, *J. Am. Chem. Soc.*, **69**, 1339 (1947).

[10] Y. Pocker, F. Naso, and G. Tocchi, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[11] K. N. Campbell and M. J. O'Conner, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

The aqueous fraction was extracted with pentane, and the two organic fractions combined and dried over anhydrous magnesium sulfate. The solution was filtered and the pentane removed; v.p.c. analysis of the residue (68 g.) indicated that it was 70% *cis*-1-phenylpropene. Fractionation at 80 mm. gave a center cut, b.p. 95–96°, analyzing as 99.8% *cis*-1-phenylpropene.

1- and 2-Bromo-1-phenylpropane.—Preliminary experiments were carried out with hydrogen bromide in order to establish the optimum conditions for the polar addition reaction. It was found that, when 5.0 ml. of pentane was placed in a reaction flask immersed in an ice bath, 1.0 ml. of *trans*-1-phenylpropene added, and hydrogen bromide passed in while irradiating the mixture with a G.E. sun lamp at 6 in. from the reaction flask, 2-bromo-1-phenylpropane was obtained essentially quantitatively. On the other hand, when the addition was carried out as described below for deuterium bromide, only 1-bromo-1-phenylpropane was obtained. With no precautions, mixtures of the two isomers were obtained.

Addition of Deuterium Bromide to 1-Phenylpropene.—In a typical reaction 5 ml. of methylene chloride containing 0.05 g. of 2,6-di-*tert*-butylphenol was placed in a dry reaction flask equipped with drying tube, gas inlet tube, and syringe cap. The flask was immersed in an ice bath, light excluded, and the solution saturated with deuterium bromide. 1-Phenylpropene (2.5 ml.) was added. Deuterium bromide was passed into the reaction mixture in a steady stream to maintain a saturated solution throughout the course of the reaction. After the desired reaction interval (complete reaction required about 50 min.), the flask was transferred to a rotary evaporator and the excess deuterium bromide and methylene chloride removed under vacuum. The residue was analyzed by n.m.r. and found to be free of unreacted olefin and free-radical addition product. Peaks corresponding to 2,6-di-*tert*-butylphenol and a trace of methylene chloride were present. The product bromide was stored in a sealed ampoule at Dry Ice temperature.

Dehydrobromination of 1-Bromo-1-phenylpropane-2-d_1.—Attempts to carry out dehydrobromination with potassium ethoxide in ethanol proved unsatisfactory owing to the formation of appreciable amounts of ether as a side product. However, elimination with potassium *tert*-butoxide in *tert*-butyl alcohol gave complete conversion to olefin. The samples obtained from addition of deuterium bromide were added to a 2–3 mole excess of 1.0 M potassium *tert*-butoxide in *tert*-butyl alcohol at 80° and stirred for 2–5 hr., the longer reaction times being required for the product of addition to *cis*-1-phenylpropene. At the end of the reaction period the reaction mixture was dumped into ice water and extracted twice with pentane. The pentane layers were combined, washed with dilute hydrochloric acid, washed with water, and dried over anhydrous sodium carbonate. After filtration, the pentane was removed on a rotary evaporator, leaving a yellow oil. Completeness of reaction was checked by n.m.r., and v.p.c. analysis of the crude product gave the amounts of *cis*- and *trans*-1-phenylpropene present. Only a few per cent of side reaction was found to occur in the elimination. Pure *trans*-1-phenylpropene was isolated by preparatory v.p.c. Attempts to collect pure samples of the small amounts of *cis*-olefin formed in these eliminations were not successful. The samples of *trans*-1-phenylpropene obtained were submitted for mass spectral analysis.

Isomerization of 1-Bromo-1-phenylpropane-2-d_1 under the Reaction Conditions.—A sample of the deuteriobromide of *trans*-1-phenylpropene determined to be free of unreacted olefin was divided into two parts; one was dehydrobrominated and the product analyzed (found 85.0% of deuterated *trans*-olefin), and the other was treated under the reaction conditions for addition of deuterium bromide described above. The material isolated at the end of a period comparable to the longest reaction time employed in any addition experiment gave an n.m.r. spectrum identical with that obtained from the sample prior to the reaction. This material was dehydrobrominated and analyzed (found 85.1% deuterated *trans*-olefin).

Isomerization of 1-Phenylpropenes under the Reaction Conditions.—Addition experiments were carried out as described above but stopped prior to completion of the reaction. In experiments with *trans*-1-phenylpropene the reaction mixture could be analyzed directly by v.p.c. The analysis was complicated by the fact that 1-bromo-1-phenylpropane in the reaction product thermally eliminated on the injection port forming predominantly *trans*-1-phenylpropene. By using reduced injection port temperatures, the amount of elimination could be minimized, and, standardizing the v.p.c. procedure with known samples of bromide and olefin, reproducible results were obtained. This v.p.c. procedure could not be satisfactorily used to estimate small amounts of *trans*-olefin (less than 10%) in the presence of bromide and *cis*-olefin so that it became necessary to find an alternate procedure to determine the extent of isomerization accompanying addition to *cis*-1-phenylpropene. Here n.m.r. analysis proved satisfactory, for characteristic peaks for the two isomers were distinguishable in the olefinic proton region of the spectra. Spectra were run on synthetic mixtures covering the range of interest, and peak height measurements were used as a measure of the composition.

In other experiments the reaction product obtained from incomplete addition was added to 7 ml. of pyridine at 50° and allowed to stand 10 hr. The mixture was then diluted with pentane and extracted three times with dilute hydrochloric acid. The organic fraction was dried over anhydrous sodium carbonate, filtered, and the pentane evaporated. Nuclear magnetic resonance analysis of the residue showed that all the bromide had been removed as the pyridinium salt. This material was purified by v.p.c. to obtain pure olefin which was checked for deuterium content by mass spectral analysis. In experiments with *cis*-1-phenylpropene, no deuterium incorporation was found in the recovered *cis*-olefin. With *trans*-1-phenylpropene 0.6% of monodeuterated *trans*-olefin was found in the recovered *trans*-olefin.

Relative Rate of Addition.—An addition was carried out with hydrogen bromide as described above for deuterium bromide, but equal amounts (0.5 ml.) of *cis*- and *trans*-1-phenylpropene were used, and the reaction was stopped short of completion (40 ± 4% reaction). The reaction product was analyzed by v.p.c. (precautions outlined in the previous section were observed). The composition of the unreacted olefin was found to be *trans/cis* = 1.09 ± 0.05, indicating that the *cis*-olefin reacts 8–29% faster than the *trans* isomer.

V.p.c. Analysis.—Analytical v.p.c. measurements were performed on an Aerograph Model 600 gas chromatograph using an 8 ft. × $^{1}/_{8}$ in. column packed with 20% diethylene glycol succinate on Chromosorb P. The column was operated at 150° with a flow of 25 ml. nitrogen per minute. Retention times were: *cis*-1-phenylpropene, 4.0 min.; *trans*-1-phenylpropene, 5.0 min. All analyses reported herein were based on calibrations with known mixtures.

Preparatory v.p.c. was carried out on an F and M Model 500 gas chromatograph with a 7 ft. × 0.5 in. column packed with 30% diethylene glycol succinate on Chromosorb P. Column temperature was 150°, and a helium flow of about 1000 ml. per minute was used. Retention times were: *cis*-1-phenylpropene, 6.2 min.; *trans*-1-phenylpropene, 7.8 min.

N.m.r. Spectra.—All n.m.r. spectra were run on a Varian V-4300-B spectrometer operating at 40 Mc./sec. Since n.m.r. was used here to establish purity of samples, all samples were measured as pure liquids to allow optimum sensitivity in the detection of impurities. For purposes of comparison, samples were also run as 20% v./v. solutions in carbon tetrachloride with TMS as internal standard. The results are summarized below.

Chemical shift, τ	Relative intensity	Splitting	Assignment
		trans-1-Phenylpropene	
2.83	5.0	Narrow multiplet	Aromatic
3.75	2.0	Narrow multiplet	Olefinic
8.13	2.9	Doublet, J 5 c.p.s.	Methyl
		cis-1-Phenylpropene	
2.79	5.0	Narrow multiplet	Aromatic
3.4 to 4.7	2.0	Complex multiplet	Olefinic
8.14	3.1	Doublet of doublets, J 7 and J' 1 c.p.s.	Methyl
		2-Bromo-1-phenylpropane	
2.82	5.0	Narrow multiplet	Aromatic
5.88	0.9	Quintuplet, J 7 c.p.s.	C_2–H
6.86	1.7	Doublet, J 6 c.p.s.	C_1–H
6.93		Doublet, J 8 c.p.s.	
8.36	2.9	Doublet, J 6.5 c.p.s.	Methyl
		1-Bromo-1-phenylpropane	
2.75	5.0	Narrow multiplet	Aromatic
5.25	1.0	Triplet, J 7 c.p.s.	C_1–H
7.82	2.2	Approx. quintuplet, J 7 c.p.s.	C_2–H
9.03	3.1	Triplet, J 7 c.p.s.	Methyl

The deuteriobromides gave similar spectra to the corresponding hydrobromides cited above, but splitting was of lower order and the peaks were broadened as expected for the deuterium substitution. The C_1–H resonance of 2-bromo-1-phenylpropane appears as two doublets indciating that the two C_1-protons are nonequivalent, their chemical shifts averaging to slightly different values under rapid rotation about the C_1–C_2 bond. Values for per cent reaction quoted here were based on integrated intensities of the olefinic resonance as compared with that of the characteristic peaks for the bromide.

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