A Mechanistic Study of the Reactions of 1,2-Disubstituted Alkenes with Hydrogen Bromide in Acetic Acid[1]

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Abstract: The stereochemistry and kinetics of the addition reactions of hydrogen bromide and acetic acid to *cis*- and *trans*-2-butene and 3-hexene and cyclopentene in hydrogen bromide–acetic acid have been studied. The stereochemistry of the addition of deuterium bromide and acetic acid-*O*-*d* to *cis*- and *trans*-2-butene occurs 84 ± 2% anti, is invariant over a 100-fold concentration range of deuterium bromide, and is unaffected by the presence of added lithium bromide or lithium perchlorate. The stereochemistry of the addition reactions to *cis*- and *trans*-3-hexene is 84–85% anti. The stereochemistry of the addition reactions to cyclopentene is 96 ± 4% anti (no syn addition product detected by ir techniques) and is not altered on change in the concentration of deuterium bromide or by the presence of added lithium bromide or perchlorate. The kinetics of the reaction of cyclopentene with hydrogen bromide in acetic acid appear to obey the kinetic expression $-d[alkene]/dt = k_{RB_r}[alkene][HBr]^2 + k_{ROAc}[alkene][HBr]$ in which alkyl bromide is derived only from the third-order term and alkyl acetate is derived only from the second-order term. k_{RB_r} and k_{ROAc} vary slightly with change in the initial concentration of hydrogen bromide, the rate constants decreasing with decreasing hydrogen bromide and cyclopentene concentration; however, the rate expression appears to remain the same. This phenomenon is attributed to changes in the reaction medium with change in hydrogen bromide concentration. The hydrogen–deuterium kinetic isotope effect is found to be 0.48 ± 0.02 for cyclopentyl bromide formation and 0.63 ± 0.07 for cyclopentyl acetate formation. The effect of added lithium bromide and lithium perchlorate on the rate of reaction has been determined and is discussed. A mechanism for the addition reactions is proposed involving syn and anti AdE3 transition states in which the hydrogen ion is delivered to the carbon by undissociated hydrogen bromide as the nucleophilic portion of the addends is delivered to the β carbon.

The electrophilic addition of the hydrogen halides to alkenes has received considerable attention; however, the intimate details of the addition mechanisms have been studied for only a very few systems.[3] The stereochemistry of the electrophilic addition of hydrogen chloride and hydrogen bromide to a few cyclic conjugated and nonconjugated alkenes has been determined, but accompanying kinetic investigations have been carried out in only a few of these studies. In general, conjugated alkenes undergo dominant syn addition of the hydrogen halides, whereas nonconjugated alkenes undergo dominant anti addition of the hydrogen halides.

The electrophilic addition of hydrogen bromide to cyclohexene,[4] 1,2-dimethylcyclohexene,[5a] and 1,2-dimethylcyclopentene[5b] occurs predominantly anti. A free carbonium ion was not implicated as an intermediate in the hydrobromination of 1,2-dimethylcyclohexene since 1,2-dimethylcyclohexene, 1,6-dimethylcyclohexene, and 2-methylmethylenecyclohexane, which should lead to the formation of the same carbonium ion intermediate, produced different kinetically controlled proportions of *cis*- and *trans*-1,2-dimethylbromocyclohexane. The transition state for the rate-determining step was proposed to involve the simultaneous formation of the carbon–hydrogen and carbon–bromine bonds, either in a converted process or by attack by bromide ion on a preformed proton–alkene complex. Dewar and Fahey[6] later suggested that the observed stereochemistry of the hydrogen bromide addition to 1,2-dimethylcyclohexene could be explained by methyl–methyl eclipsing torsional effects encountered in the conversion of the 1,2-dimethylcyclohexyl carbonium ion to the cis dimethyl product, which would be absent in the formation of the trans dimethyl product.

In contrast to the observed stereochemistry of the addition of hydrogen bromide to the nonconjugated, cyclic alkenes, hydrogen bromide undergoes predominantly syn addition to the conjugated alkenes acenaphthalene,[7] indene,[6] and 1-phenylpropene.[8] The mechanism of the addition of hydrogen bromide to these alkenes was proposed to proceed *via* formation of a carbonium ion–chloride ion tight ion pair which collapsed to the syn addition product.

Very few kinetic studies of the addition of hydrogen bromide to alkenes have been carried out. The addition in pentane appears to be fourth order overall; first order in alkene and third order in hydrogen bromide.[9] The reaction appears to be faster and of a lower kinetic order in ether and hydroxylic solvents.[9]

The majority of the kinetic studies of hydrogen halide additions has been concerned with the addition of hydrogen chloride to alkenes in acetic acid and nitromethane. The reactions of hydrogen chloride with alkenes in acetic acid appears to be a rather complex reaction, resulting in the syn and anti addition of hy-

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(2) Du Pont Teaching Fellow 1968–1969; Lubrizol Research Fellow, 1969–1970. Submitted in partial fulfillment of the requirements of the Ph.D. degree, University of Notre Dame, 1970.

(3) For a recent review, see R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(4) R. C. Fahey and R. A. Smith, *J. Amer. Chem. Soc.*, **86**, 5035 (1964).

(5) (a) G. S. Hammond and T. D. Nevitt, *J. Amer. Chem. Soc.*, **76**, 4121 (1954); (b) G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

(6) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2248 (1963).

(7) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **84**, 2012 (1962); **85**, 2245 (1963).

(8) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 3645 (1963).

(9) F. R. Mayo and M. G. Savoy, *J. Amer. Chem. Soc.*, **69**, 1348 (1947).

drogen chloride and acetic acid to the alkene,[10] with the reactions following complex kinetic expressions. Hydrogen–deuterium kinetic isotope effects of 1.3–1.4 were measured.[10] The kinetics of the addition of hydrogen chloride to alkenes in nitromethane have been found to be overall third order; first order in alkene and second order in hydrogen chloride (k_H/k_D = 0.61 for 1-methylcyclopentene).[11]

Preliminary studies in our laboratories[12] revealed that the electrophilic addition of deuterium bromide to *cis*- and *trans*-2-butene in ~1 *M* deuterium bromide in acetic acid-*O-d* at room temperature proceeded predominantly anti (85%). In view of the synthetic importance of electrophilic addition reactions, and the lack of prior studies concerning the mechanism of hydrogen bromide addition reactions, we initiated a more detailed study of the mechanistic details of the electrophilic addition of hydrogen bromide to nonconjugated, unstrained alkenes in acetic acid.

Results

Stereochemistry of Addition of Deuterium Bromide and Acetic Acid-*O-d*: *cis*- and *trans*-2-Butene. Preliminary experiments involving the addition of deuterium bromide to *cis*- and *trans*-2-butene in acetic acid-*O-d* in the presence of typical radical inhibitors and subject to the laboratory atmosphere and light produced identical mixtures of 60% *threo*- and 40% *erythro*-3-deuterio-2-bromobutane.[12] Interruption of the reactions prior to the total consumption of the alkene followed by recovery of the unreacted 2-butene by trap-to-trap distillation and analysis by glpc showed that isomerization of the 2-butene had occurred (cis $\rightleftarrows$ trans K_{eq} = 2.80 at 25°). Qualitative experiments showed that the rate of alkene isomerization was considerably greater than the rate of addition to either *cis*- or *trans*-2-butene indicating that the stereochemical composition of the product mixtures could not be directly related to the stereochemistry of the addition of deuterium bromide to the individual alkenes. The alkene isomerization was shown not to be acid catalyzed as indicated by the fact that no hydrogen–deuterium exchange occurred between the alkene and the solvent, and the observation that alkene isomerization did not occur at a detectable rate at 40° in the presence of comparable concentrations of hydrogen chloride, *p*-toluenesulfonic acid, or sulfuric acid in acetic acid. In a series of experiments it was shown that hydrogen ion, bromide ion, and oxygen or light was required for the alkene isomerization. It was concluded, therefore, that the alkene isomerization was caused by the presence of bromine atoms in solution which are formed according to

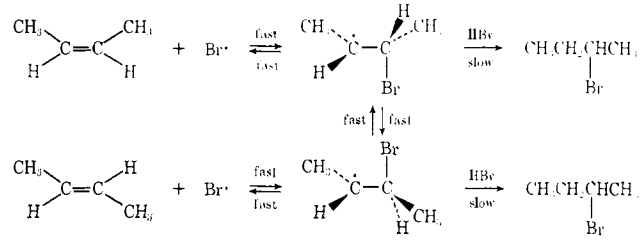
$$HBr + O_2 \longrightarrow HOO\cdot + Br\cdot$$

$$HBr \xrightarrow{h\nu} H\cdot + Br\cdot$$

The isomerization occurs by the fast and reversible addition of a bromine atom to the alkene to form a β-bromoalkyl radical of sufficient lifetime such that rotational isomerization can take place. The alkene isomerization reaction could be stopped only when the hydrogen bromide–acetic acid solutions were triply freeze degassed and the alkene added under an argon or helium atmosphere, and with the reaction being carried out in the dark. (The presence of even large excesses of typical radical inhibitors did not quench the alkene isomerization reaction.)[13] The stereochemical studies reported herein were obtained at 25 ± 0.1° using a 1.5:1 molar ratio of alkene–deuterium bromide. The reactions were allowed to proceed to ≳95% consumption of the deuterium bromide. An aliquot of the reaction mixture was quenched with *N,N*-dimethylaniline and analyzed directly by glpc to determine the alkyl bromide–alkyl acetate ratio. The remaining portion of the reaction mixture was subjected to a trap-to-trap distillation to recover the unreacted alkene. The cis–trans composition of the recovered alkene was determined by glpc. The stereochemical results discussed hereafter are for those reactions in which *no* alkene isomerization was detected.[15]

Table I. Reaction of 2-Octene with Hydrogen Bromide in Acetic Acid in the Presence of an Oxygen Atmosphere

[HBr] = [2-octene], *M*	Mol % O_2 uptake	% yield alkyl bromide	% yield alkyl acetate
1.25	50.3	44.5	9.7
0.40	60.4	16.7	8.1
0.20	82.7	9.0	4.3



Thus, the direction of addition of hydrogen bromide to unsymmetrically substituted alkenes in solution is not a sensitive probe for the detection of the presence of radical reactions, such as that leading to isomerization but not addition. Only in the presence of fairly high concentrations of benzoyl peroxide, or when the reaction mixtures are maintained under an oxygen atmosphere, is 1-bromobutane formed in significant quantities (but not as the sole product). It is also interesting to note that oxygen can both initiate the bromine atom catalyzed isomerization reaction as well as react with the intermediate radicals that are formed. When the solution of an alkene and hydrogen bromide in acetic acid is rapidly stirred under an atmosphere of oxygen, oxygen is consumed (see Table I for the case of 2-octene) and the yield of alkyl bromide drops precipitously. Analysis of the oxygenated product mixtures by glpc indicated the formation of many products, all in very low yield. In view of the complexity of the product mixtures and the fact that the liquid phase oxidation of alkenes has been extensively studied,[16] this reaction was not further investigated.

(10) (a) R. C. Fahey and M. W. Monahan, *Chem. Commun.*, 936 (1968); (b) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, 92, 2810 (1970); (c) R. C. Fahey and M. W. Monahan, *ibid.*, 92, 2816 (1970); (d) R. C. Fahey and C. A. McPherson, *ibid.*, 91, 3865 (1969).

(11) Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Amer. Chem. Soc.*, 91, 4199 (1969); Y. Pocker and K. D. Stevens, *ibid.*, 91, 4205 (1969).

(12) D. J. Pasto, G. R. Meyer, and S.-Z. Kang, *J. Amer. Chem. Soc.*, 91, 2163 (1969).

(13) Fahey and coworkers have similarly observed that the presence of radical inhibitors in these reactions does not suppress competitive radical reactions.[14]

(14) R. C. Fahey, C. A. McPherson, and R. A. Smith, submitted for publication.

(15) Interestingly, when a mixture of *cis*-3-hexene and 1-butene was treated with hydrogen bromide in acetic acid under conditions where alkene isomerization occurred, the bromine atom catalyzed isomerization of *cis*-3-hexene occurred very rapidly, but *no* 1-butene radical chain addition product, 1-bromobutane, was formed. Apparently, only a very low concentration of the β-bromoalkyl radical is formed, from which the radical chain addition process or the reaction with a radical inhibitor or trap cannot successfully compete with the intramolecular loss of bromine atom to regenerate the alkene; *i.e.*

(16) F. R. Mayo, *J. Amer. Chem. Soc.*, 80, 2497 (1958), and references cited therein.

The alkyl bromide and acetate were isolated by the addition of water to the reaction mixture followed by extraction with pentane, and were separated and purified by preparative glpc. The nmr spectra of the individual bromide fractions derived from *cis*- and *trans*-2-butene indicated that mainly one diastereoisomer of 3-deuterio-2-butyl bromide was obtained from each alkene. The assignment of the stereochemistry of the dominant diastereoisomer derived from each alkene was accomplished by conversion of the bromide fractions to the corresponding 3-deuterio-2-butyl benzoates by treatment with silver benzoate–sodium benzoate in hexamethylphosphoramide and comparison of the infrared spectra of the benzoates with the spectra of authentic samples and mixtures of known composition of *erythro*- and *threo*-3-deuterio-2-butyl benzoates previously prepared in our laboratories.[17] After identification of the stereochemistry of the dominant diastereoisomer in the bromide mixtures, the stereochemical composition of the bromide fractions was determined by direct integration of the resonance lines of CHBr of the bromide fractions employing deuterium decoupling at −60° in deuteriochloroform solution, or at 40° in benzene solution.[18] The alkyl bromide was indicated to be stereochemically stable under the reaction conditions as evidenced by the lack of change of stereochemical composition of the alkyl bromide with varying reactions times, and by the fact that optical rotation of a solution of optically active 2-octyl bromide in hydrogen bromide–acetic acid remained constant during the course of the addition reaction.

The stereochemical composition of the 2-butyl acetate was determined by conversion to the benzoate (reduction with lithium aluminum hydride followed by benzoylation with benzoyl chloride in pyridine) and analysis by infrared spectroscopy.

The stereochemistry of the addition of deuterium bromide and acetic acid-*O*-*d* to *cis*- and *trans*-2-butene was determined over an approximate 100-fold initial concentration range of deuterium bromide, as well as in the presence of added lithium bromide and lithium perchlorate. These data are presented in Table II, along with the bromide–acetate product ratios which were determined directly by glpc.

***cis*- and *trans*-3-Hexene.** The 3-hexyl bromide and acetate fractions derived from *cis*- and *trans*-3-hexene were separated and purified by preparative glpc. *No* 2-hexyl derivatives were detected by analytic glpc techniques. The nmr spectra of the 3-hexyl bromide fractions did not differ sufficiently to allow direct determination of the stereochemical composition by integration of the –CHBr– resonance region. The bromides were converted to the benzoates (silver benzoate–sodium benzoate in HMPA) and analyzed by integration of the –CHOBz– region in benzene solution at 40°.

The assignment of the stereochemistry of the dominant benzoate diastereoisomer was made by comparison of the nmr spectral properties with those of authentic *erythro*-4-deuterio-3-hexyl benzoate prepared by the deuterioboration of *cis*-3-hexene followed by oxidation, hydrolysis, and benzoylation. The stereoselectivity of the addition of deuterium bromide to *cis*- and *trans*-3-hexene was found to be 84–85% anti. The stereochemistry of the addition of acetic acid-*O*-*d* to *cis*- and *trans*-3-hexene was determined (*vide infra*) to be 84–85% anti.

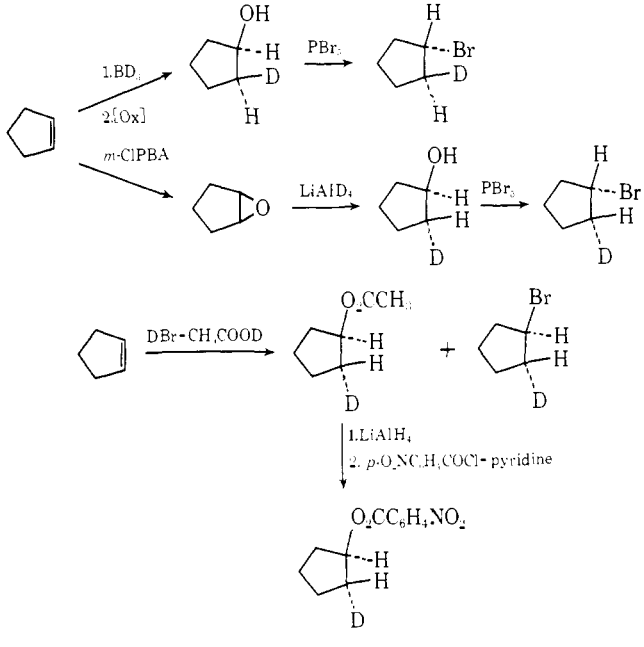
Table II. Stereochemistry of Products and Product Ratios Derived in the Reactions of *cis*- and *trans*-2-Butene with Deuterium Bromide in Acetic Acid-*O*-*d*[a]

Alkene	[DBr], *M*	Salt (*M*)	Alkyl acetate; erythro isomer (% of total acetate)	Alkyl bromide; erythro isomer (% of total bromide)	RBr–ROAc ratio[b]
cis-2-Butene	0.03		*c*	17	*c*
cis-2-Butene	0.14		15	17	4.07
cis-2-Butene	0.77		*c*	15	*c*
cis-2-Butene	1.06		18	18	9.00
cis-2-Butene	3.24		15	15	10.1
trans-2-Butene	0.60		85	85	*c*
trans-2-Butene	1.26		85	87	*c*
trans-2-Butene	2.56		82	85	*c*
trans-2-Butene	0.80	LiBr (0.161)	*c*	82	24.4
trans-2-Butene	0.80	LiBr (0.798)	*c*	84	30.8
trans-2-Butene	0.80	$LiClO_4$ (0.160)	*c*	82	6.9
trans-2-Butene	0.80	$LiClO_4$ (0.800)	*c*	83	6.2

[a] Solutions triply freeze degassed with the reactions carried out in the dark under a helium atmosphere. Analysis of recovered unreacted alkene by glpc showed that no isomerization of the starting alkene had occurred. [Alkene] = 1.5[DBr]. [b] Integrated product ratios over >95% reaction of the alkene. [c] Not determined.

Cyclopentene. Authentic samples of *cis*- and *trans*-2-deuteriocyclopentanol and cyclopentyl bromide were prepared according to reaction Scheme I. The conversion of the *cis*- and *trans*-2-deuteriocyclopentanols to the *trans*- and *cis*-2-deuteriocyclopentyl bromides, respectively, with phosphorus pentabromide,[16] occurred with >96% inversion (limit of detection by ir

Scheme I



(17) D. J. Pasto, C. C. Cumbo, and J. Hickman, *J. Amer. Chem. Soc.*, 88, 2201 (1966).

(18) Comparison of the nmr and ir analyses indicated that the transformation of the bromides to the benzoates occurred with complete inversion.

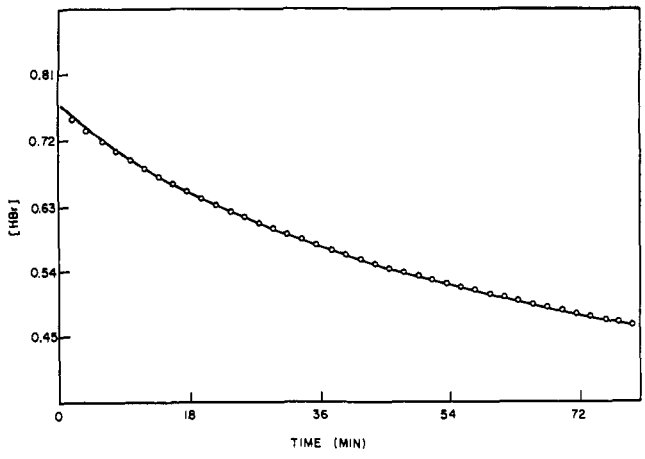


Figure 1. Calculated (—) and experimental (O) hydrogen bromide concentration in the reaction of cyclopentene with hydrogen bromide in acetic acid following eq 1 rate law.

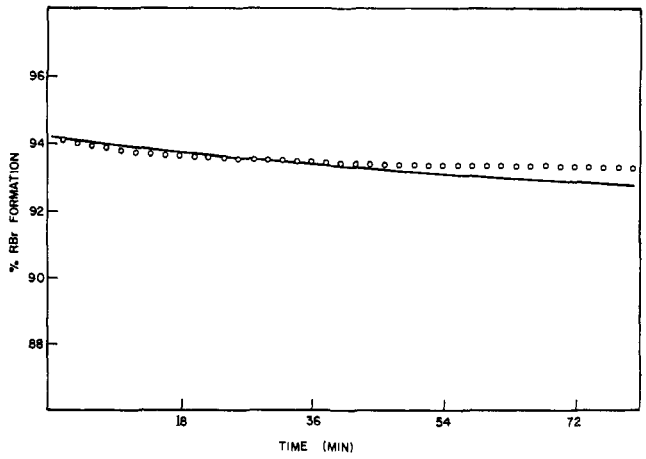


Figure 2. Calculated (—) and experimental (O) product compositions corresponding to the rate data in Figure 1.

techniques) as indicated by comparison of the infrared spectra of the isomeric 2-deuteriocyclopentyl bromides and the benzoates of the starting alcohols (inversion of configuration was assumed on the basis of analogy).[19] The stereochemical composition of the 2-deuteriocyclopentyl bromide fractions derived from the reactions of cyclopentene with deuterium bromide in acetic acid-*O-d* was determined by comparison of the ir spectra of the cyclopentyl bromide fractions with the ir spectra of mixtures of known composition of *cis*- and *trans*-2-deuteriocyclopentyl bromide. In all cases *no* bands corresponding to the *cis*-2-deuteriocyclopentyl bromide could be detected, and we conclude that the addition of deuterium bromide to cyclopentene occurs at least in a >96% manner (see Table III).

Table III. Stereochemistry of the Addition of Deuterium Bromide and Acetic Acid-*O-d* to Cyclopentene[a]

[DBr], *M*	Cyclopentyl bromide; % anti addition	Cyclopentyl acetate; % anti addition	RBr–ROAc[b]
0.20	>96	>96	5.88
0.75	>96	>96	8.34
1.20	>96	>96	16.7

[a] [Alkene] = 1.5[DBr]. [b] Integrated product ratio over >95% reaction.

The stereochemistry of the addition of acetic acid-*O-d* to cyclopentene was determined by ir techniques on the corresponding *p*-nitrobenzoates which were prepared from the acetates (*vide infra*).

Kinetic Measurements. The rate of reaction of cyclopentene[20] with hydrogen bromide in acetic acid[21] was followed by periodic potentiometric titration of aliquots of the reaction mixtures. The alkyl bromide–alkyl acetate product ratios were determined by glpc analysis of aliquots quenched with *N,N*-dimethylaniline. The reactions were monitored to 30–50% completion.

The kinetic data were analyzed by a directed-minimization computer program in which a number of different kinetic expressions were evaluated. With each kinetic expression the change in hydrogen bromide concentration [HBr] and alkyl bromide–alkyl acetate (RBr–ROAc) product ratio were calculated as a function of time where the intervals Δt approximated 0.025–0.1% of the total reaction time. The rate constants were varied in a systematic manner until the best least-squares fits of the calculated and final values of [HBr] and RBr:ROAc ratio were obtained. The rate expression which produced the best fit of the calculated and experimental data is

$$-d[C_5H_8]/dt = k_{RBr}[C_5H_8][HBr]^2 + k_{ROAc}[C_5H_8][HBr] \quad (1)$$

in which alkyl bromide is formed *only* in the third-order process and alkyl acetate *only* in the second-order process.[22] Reproductions of computer generated plots of hydrogen bromide concentration and per cent alkyl bromide formed *vs.* time are shown in Figures 1 and 2. The correspondence between the calculated and experimental data is well within the experimental errors of the techniques used to monitor the course of the reaction. The rate constants for reactions involving the same initial concentrations of cyclopentene but differing in initial hydrogen bromide concentration follow the rate expression (1) within experimental error out to 30–50% reaction; however, the calculated rate constants are not constant in value, both k_{RBr} and, in particular, k_{ROAc} decrease with decreasing hydrogen bromide concentration (Table IV).

Rate data for the reaction of cyclopentene with hy-

(19) E. L. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, 81, 147 (1959).

(20) Several attempts were made to follow the rates of the reactions of *cis*- and *trans*-3-hexene; however, during the course of monitoring the rate of reaction (see Experimental Section) slow alkene isomerization occurred complicating the analysis and interpretation of the results.

(21) The use of commercially available glacial acetic acid led to very erratic results; the rates of reaction being two to four times the rate of reaction in acetic acid prepared as described in the Experimental Section. Acetic acid-*O-d* was prepared in a similar manner.

(22) Other kinetic expressions evaluated are

$$-d[C_5H_8]/dt = k_{RBr}[C_5H_8][HBr]^n + k_{ROAc}[C_5H_8][HBr]^m$$

where n was varied from 1.0 to 2.4 and m from 1.0 to 2.0

$$-d[C_5H_8]/dt = k_{RBr}[C_5H_8][HBr]^2 + k'_{RBr}[C_5H_8][HBr] + k_{ROAc}[C_5H_8][HBr]$$

and

$$-d[C_5H_8]/dt = k_{RBr}[C_5H_8]H_0^n + k_{ROAc}[C_5H_8]H_0^m$$

where n was varied from 1.0 to 2.4, m from 1.0 to 2.0, and H_0 is the acidity function for hydrogen bromide in acetic acid determined in this study.

Table IV. Rate Constants for the Reactions of Cyclopentene with Hydrogen Bromide in Acetic Acid at 25°

[HBr],[a] M	[CP],[a] M	k_{RBr}, l.[2] mol^{-2} min^{-1}	k_{ROAc}, l. mol^{-1} min^{-1}
0.80[b]	0.80	0.0192	0.0009
0.80[b]	0.80	0.0202	0.0011
0.80 (DBr)[b]	0.80	0.0410	0.0016
0.80 (DBr)[b]	0.80	0.0406	0.0016
0.40	0.80	0.0165	0.00085
0.40	0.80	0.0130	0.0006
0.19	0.21	0.0169	0.00023

[a] Initial reactant concentrations. Reactions followed in general to 30–50% completion; see ref 28. [b] Duplicate kinetic runs using the same batch of acetic acid (or acetic acid-*O*-*d*).

drogen bromide in acetic acid in the presence of added lithium bromide and lithium perchlorate were also measured. The rate of disappearance of hydrogen bromide at short reaction times was accelerated (by a factor of 2–3 in the presence of 0.32 M salt) in the presence of *both* lithium bromide and lithium perchlorate; however, the rate of reaction in both cases appeared to be retarded at longer reaction times as calculated by expression 1. The integrated alkyl bromide–acetate ratio increased substantially in the presence of added lithium bromide, and decreased in the presence of added lithium perchlorate (see Table V). Attempts at fitting

Table V. Product Ratios for the Reactions of 0.70 M Cyclopentene with 0.70 M Hydrogen Bromide in Acetic Acid in the Presence of Added Lithium Bromide and Lithium Perchlorate

Added salt	M	RBr–ROAc ratio	% RBr
a		8.34	89.3
LiBr	0.06	12.2	92.3
LiBr	0.13	12.2	92.3
LiBr	0.32	12.5	92.7
LiBr	0.64	13.7	93.2
$LiClO_4$	0.32	6.42	86.6

[a] Initial concentration of hydrogen bromide and cyclopentene 0.75 M in absence of added salt.

the experimental data of the reactions carried out in the presence of the lithium bromide to various kinetic expressions incorporating lithium bromide concentration dependent terms were unsuccessful. Attempts at correlating the rate data derived in the presence of lithium perchlorate were also fruitless.

Discussion

Stereochemical Considerations. Various mechanistic processes for electrophilic additions to alkenes, and their anticipated stereochemistries have been discussed in a review by Fahey.[3] In the present case the competing syn and anti addition reactions of *cis*- and *trans*-2-butene and 3-hexene with hydrogen bromide in acetic acid can be rationalized by: (1) an AdE2-type process involving the formation of a carbonium ion–bromide ion tight ion pair which collapses to syn addition product, or rearranges to produce anti addition product; (2) competing syn AdE2 and anti AdE3 processes; or (3) competing syn and anti AdE3 addition reactions. A distinction between these three alternatives can be made on the basis of stereochemical results derived under differing initial concentrations of hydrogen bromide, the effect of added salts on the stereochemical course of the addition reactions, and by the results of kinetic studies.

In a reaction proceeding *via* the first pathway, the stereochemistry of the addition of hydrogen bromide should be a function of the bromide ion concentration, particularly when the bromide ion concentration is increased by the addition of a neutral salt while maintaining the hydrogen ion concentration constant.[23] In the present study such is not the case. Although a change in the alkyl bromide–acetate product ratio is observed, the lack of an effect of added lithium bromide on the stereoselectivity of the addition of deuterium bromide to *cis*- and *trans*-2-butene suggests that alkyl bromide formation does not occur *via* the first pathway. The higher than first-order dependence of alkyl bromide formation on hydrogen bromide concentration also militates against an AdE2-type process, although a similar type intermediate, *i.e.*, a carbonium ion–hydrogen dibromide ion tight ion pair, can be visualized as being formed in a third-order process. This mechanistic possibility, however, cannot be operative in view of the lack of retardation in the rate of reaction and the lack of an effect of added bromide salt on the stereoselectivity of the addition reaction.

The second pathway can be eliminated on the basis of the stereochemical results obtained with *cis*- and *trans*-2-butene. In such a case the kinetic expression for the formation of alkyl bromide (eq 2) leads one to predict that at high concentrations of hydrogen bromide the third-order term should be dominant, whereas at lower concentrations the second-order term should become relatively more important. Thus, if the stereochemistry

$$+\mathrm{d[RBr]}/\mathrm{d}t = k_2[\text{alkene}][\mathrm{HBr}] + k_3[\text{alkene}][\mathrm{HBr}]^2 \quad (2)$$

involved in product formation from the two terms is different, a not unreasonable assumption postulated earlier,[3] the overall stereochemistry of the addition reaction must be a function of the initial concentration of the hydrogen bromide. Such a stereochemical dependence must be apparent providing that one of the kinetic terms does not overwhelm the other in product formation. This would not appear to be the case with the *cis*- and *trans*-2-butenes in which a stereoselectivity of 84 ± 2% is observed. Thus, a 100-fold change in initial deuterium bromide concentration would be expected to result in a corresponding 100-fold change in the relative contributions of the two terms under the initial reaction conditions. Although in the present experiments the stereochemistry observed in the deuterium bromide addition product is an integrated average involving >95% consumption of the initial deuterium bromide, the contributions made by the second- and third-order terms to product formation at the two extremes of the deuterium bromide concentrations used is sufficiently different that the results of competitive addition processes should be easily detected. The observation that the stereochemistry of the deuterium bromide addition to the 2-butenes in invariant over a 100-fold concentration range strongly indicates that the deuterium bromide addition reaction arises from a

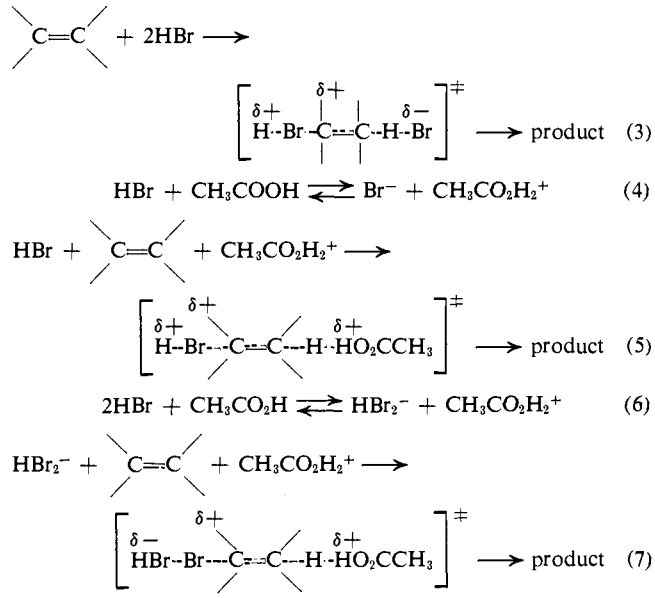
(23) This should obtain except in cases where the carbonium ion–bromide ion tight ion pair collapses to product more rapidly than it rearranges or undergoes attack by an external nucleophile. In such cases, however, only syn addition would be expected which, in the present study, is not the case.

single kinetic term and not from two competing kinetic terms of different deuterium bromide concentration dependence.

Salt Effects on the Stereoselectivity of and Possible Rearrangement Reactions. The Question of the Intervention of Tight Ion Pair Intermediates. Information regarding the nature of the transition state, or possible intermediates, formed in the deuterium bromide addition reaction can be derived by comparison with solvolysis data derived with 2-octyl tosylate.[24] The solvolysis of optically active 2-octyl tosylate in acetic acid has been proposed to proceed *via* reversible formation of a carbonium ion–tosylate ion tight ion pair.[24] The tight ion pair reverts to alkyl tosylate with 7.5% racemization (1.4 half-lives) and 0.9% rearrangement, and reacts with solvent to give alkyl acetate with >98% inversion. In the presence of added lithium perchlorate (0.1 *M*) the rate of solvolysis is enhanced (normal salt effect), and the extent of racemization and rearrangement by internal return is substantially increased (17.6 and 3.2%, respectively). In the reaction of 2-butene with deuterium bromide in acetic acid-*O-d* in the presence of lithium perchlorate an initial enhancement of the rate of addition occurs, *but the stereoselectivity of the addition does not change* (Table II). Furthermore, in the case of the addition to *cis*- and *trans*-3-hexene no rearrangement products (2-hexyl bromide or 2-hexyl acetate) were detected. We thus feel that these results are not in accord with those anticipated for the formation of a carbonium ion–anion (either bromide ion or hydrogen dibromide anion[25]) tight ion pair as an intermediate in these reactions,[27] and that these additions occur *via* concerted processes.

Kinetics of the Addition Reactions Involving Cyclopentene. The kinetic expression which best correlates the experimental data for the reaction of cyclopentene with hydrogen bromide in acetic acid contains two terms; one term first order in alkene and second order in hydrogen bromide which gives rise *only* to cyclopentyl bromide, and one term first order in both alkene and hydrogen bromide which gives rise *only* to cyclopentyl acetate. This kinetic expression is consistent with the stereochemical and product ratio data given in Table II; *i.e.*, that the syn and anti addition of hydrogen bromide occur by processes having the same kinetic order in [HBr], and that alkyl bromide and alkyl acetate are formed by processes having different kinetic orders in [HBr]. Although kinetic expression 1 correlates the experimental data at different initial concentrations of hydrogen bromide and cyclopentene within experimental error (±2% of the hydrogen bromide titrametric data and ±0.4% of the glpc product composition data), the calculated rate constants decrease slightly, but not in any direct manner with concentration, with decreasing initial concentrations of hydrogen bromide and cyclopentene. The kinetic measurements were carried out in moderately concentration solutions (0.1–0.8 *M*) of both hydrogen bromide and cyclopentene, similar to the concentrations used in the stereochemical studies and in normal preparative procedures. We believe that these changes in the rate constants reflect rather substantial changes in the properties (*i.e.*, dielectric constant) of the reaction media.

Two mechanistic possibilities exist for the transfer of a hydrogen ion to carbon in concerted addition processes which are consistent with the observed kinetics and salt effects: (1) the transfer of a hydrogen ion directly from a molecule of undissociated hydrogen bromide concomitant with attack by a bromide ion donor (*e.g.*, hydrogen bromide or lithium bromide) as in eq 3; or (2) the transfer of a hydrogen ion from a protonated molecule of solvent with concerted attack by a bromide ion donor (*e.g.*, hydrogen bromide, lithium bromide, or hydrogen dibromide anion[26]) as in eq 4 and 5, or 6 and 7.



A distinction between the two mechanistic possibilities can be made on the basis of the observed hydrogen–deuterium kinetic isotope effect data. Noyce and coworkers have studied the acid-catalyzed isomerization of *cis*- and *trans*-stilbene[28] and *cis*- and *trans*-cinnamic acid[29] in aqueous acid. These isomerization reactions involve the rate-determining protonation of carbon by hydronium ion (leading to the formation of hydration products as reaction intermediates) and are characterized by hydrogen–deuterium kinetic isotope effects in the range of 2–6. As the oxygen–hydrogen vibrational frequencies in the hydronium ion (stretching frequency of >2900 cm^{-1})[30] and protonated acetic acid should be roughly the same, the hydrogen–deuterium isotope effect for hydrogen ion transfer from protonated acetic acid should also be greater than unity. The observed isotope effect of 0.48 ± 0.02 for cyclopentyl bromide formation is thus not consistent with a mechanism in which hydrogen ion is being transferred to carbon by protonated acetic acid in the transition state (eq 4 and 5, and 6 and 7). The isotope effect of 0.48 is consistent

(24) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Amer. Chem. Soc.*, 87, 3682 (1965); A. Streitwieser, Jr., and T. D. Walsh, *Tetrahedron Lett.*, 29 (1963); *J. Amer. Chem. Soc.*, 87, 3686 (1965).

(25) All of the hydrogen dihalide anions have been characterized[26] and the consideration of such anions as possible species formed and present in such reactions must be entertained.

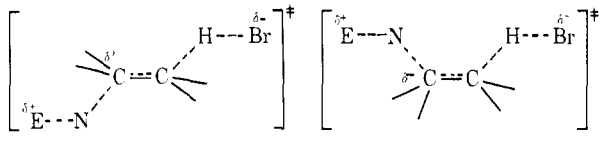
(26) J. N. Marx, *Tetrahedron Lett.*, 3517 (1970); D. H. McDaniel and R. E. Vallec, *Inorg. Chem.*, 2, 996 (1963).

(27) It is possible that carbonium ion–anion tight ion pairs are formed which exhibit different behavior from that reported by Streitwieser and Walsh;[24] however, considering the similarities of the two sets of reaction conditions, this seems doubtful.

(28) D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, 86, 3583 (1964).

(29) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Amer. Chem. Soc.*, 84, 1647 (1962).

(30) M. Falk and P. A. Giguere, *Can. J. Chem.*, 35, 1195 (1957).



anti AdE3 transition state syn AdE3 transition state

Figure 3.

with the transfer of a hydrogen ion from a species having a lower vibrational frequency than that of the carbon–hydrogen bond being formed (~2900–2850 cm^{-1}). As the stretching frequency of hydrogen bromide (2500 cm^{-1})[31] is considerably less than the vibrational frequency of the carbon–hydrogen bond being formed, the observed isotope effect is consistent with the direct transfer of hydrogen ion from undissociated hydrogen bromide to a carbon of the double bond.

Salt Effects on Reaction Rates and Product Distributions. The presence of lithium bromide initially results in a substantial increase in the rate of formation of alkyl bromide. The effect of added lithium bromide on the rate of formation of alkyl acetate appears to be negligible. Thus, the effect of lithium bromide does not appear to be simply a medium effect. Lithium bromide must act as a bromide ion donor which results in an increase in the rate of formation of alkyl bromide. Mechanisms involving prerate-determining equilibria between hydrogen bromide and solvent with protonated solvent and bromide ion, eq 4 and 6, should experience a common ion rate-retarding effect. This is not what is observed.

In the presence of added lithium perchlorate the rate of alkyl acetate formation is substantially increased while the rate of formation of alkyl bromide is only slightly increased. The rate increases may be the result of a medium effect, or due to the formation of perchloric acid which is a very effective catalyst for the

$$LiClO_4 + CH_3COOH \longrightarrow LiO_2CCH_3 + HClO_4$$

$$LiClO_4 + HBr \longrightarrow HClO_4 + LiBr$$

addition of acetic acid to norbornadiene.[32] The increased yield of alkyl acetate probably arises from less discrimination between nucleophilic species by a somewhat more developed partial charge on carbon of the π-electron system.

Acetate Formation. The identical stereochemistry of alkyl acetate formation compared to alkyl bromide formation, and the lack of formation of rearranged acetate in the reactions of *cis*- and *trans*-3-hexene, is strongly suggestive that alkyl bromide and acetate are formed in nearly identical types of transition states. The hydrogen–deuterium kinetic isotope effect of 0.63 ± 0.07 is consistent with hydrogen ion transfer to carbon from hydrogen bromide and not by protonated acetic acid.[33]

Summary

The results presented in this article suggest that the additions of hydrogen bromide and acetic acid to 1,2-dialkyl substituted alkenes occur by concerted syn and anti AdE3 processes *via* the transition states illustrated in Figure 3 in which the hydrogen ion is delivered by hydrogen bromide and E–N represents the nucleophile donors H–Br, Li–Br, or H–O_2CCH_3. Although these addition reactions are characterized as AdE3-type reactions, it is not necessary to have a termolecular collision in the transition state. A hydrogen bromide–alkene complex may be formed in a prerate-determining step equilibrium which leads to polarization of the π-electron system (*i.e.*, development of cationic character on carbon) leading to reaction with a nucleophile donor in the rate-determining step.

The alkyl bromide–alkyl acetate product ratio is determined by the relative concentrations and nucleophilicities of hydrogen bromide, lithium bromide, and acetic acid.[34] The kinetic isotope effects discussed earlier in this article are also consistent with the proposed transition states.[37]

Experimental Section

Reactions of *cis*- and *trans*-2-Butene with Deuterium Bromide in Acetic Acid-*O*-*d* under Nonisomerizing Conditions and the Stereochemical Analysis of the Products. Acetic acid-*O*-*d* (50 ml) in 100-ml round-bottomed, three-necked flask was freeze-degassed (three cycles). The reaction flask was painted black and the desired amount of deuterium bromide was generated by the slow addition of deuterium oxide to phosphorus tribromide and bubbled into the freeze-degassed acetic acid-*O*-*d* in a stream of helium. The reaction flask was fitted with a black-painted Dry Ice–acetone condenser and a solution of *cis*- or *trans*-2-butene (50% excess based on deuterium bromide concentration) dissolved in 20 ml of previously freeze-degassed acetic acid-*O*-*d* was added maintaining a helium atmosphere over the reaction mixture. The reaction was allowed to proceed to >95% completion at 25° after which time the reaction was quenched by pouring into a saturated solution of sodium acetate in acetic acid. A 15-ml aliquot of the quenched reaction mixture was subjected to a trap-to-trap distillation under reduced pressure at room temperature, the unreacted olefin being collected in a liquid nitrogen trap. The recovered olefin was analyzed by glpc on a 12-ft 15% silver nitrate–propylene glycol on Chromosorb P column at 15°. The remainder of the quenched reaction mixture was subjected to a trap-to-trap distillation. The mixture of deuteriobromide and deuterioacetate containing some acetic acid was separated by preparative glpc on a 10-ft 15% Carbowax 20M on Haloport F column at 90°. Alternatively, the quenched reaction mixture was poured into 100 ml of ether and 100 ml of distilled water contained in a separatory funnel. The organic layer was removed and the aqueous layer was extracted with ether. The combined ether extract was washed with saturated aqueous sodium bicarbonate until the evolution of carbon dioxide ceased. The ether extract was dried ($MgSO_4$) and concentrated.

(31) H. W. Thompson, R. C. Williams, and H. J. Callomon, *Spectrochim. Acta*, **5**, 313 (1952).

(32) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719, 2726 (1966).

(33) Cristol and coworkers report that the rate of the acid-catalyzed addition of acetic acid to norbornadiene is linear in acid concentration, and suggest that protonated acetic acid is the hydrogen ion donor.[32] The hydrogen–deuterium kinetic isotope effect was not determined.

(34) Hydrogen bromide and lithium bromide are only slightly dissociated in acetic acid (K_{diss} of 10^{-5}–10^{-6} for hydrogen bromide[35] and 7.2×10^{-7} for lithium bromide[36]), and thus the nondissociated species are considered to be the sources of the nucleophiles.

(35) I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.*, **78**, 1 (1956); I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934).

(36) M. M. Jones and E. Grunwald, *J. Amer. Chem. Soc.*, **76**, 3247 (1954).

(37) The hydrogen–deuterium kinetic isotope effects of 1.0–1.4 reported by Fahey[10] for the hydrogen chloride additions to alkenes are also consistent with this rationale, hydrogen chloride having a vibrational frequency (ν_{H-Cl} 2899 cm^{-1})[38] lower than that of hydronium ion, but greater than that of hydrogen bromide. The isotope effect reported for the reaction of hydrogen chloride with 1-methylcyclopentene is 0.61. This value is not consistent with a transition state similar to those proposed in the present study, but appears to be consistent with the mechanism proposed by Pocker in which the second molecule of hydrogen chloride weakens the hydrogen–chlorine bond of the proton donating hydrogen chloride by hydrogen bonding leading to the formation of a carbonium ion–hydrogen dichloride anion tight-ion pair.[11]

(38) I. M. Mills, H. W. Thompason, and R. C. Williams, *Proc. Roy. Soc., Ser. A*, **218**, 29 (1953).

The residue was separated by preparative glpc using a 7-ft 15% Carbowax 20M on Chromosorb W column at 90°.

The ir spectra of the 3-deuterio-2-bromobutanes obtained from the addition of deuterium bromide to *cis*- and *trans*-2-butene were indistinguishable. The nmr spectra of the bromide fractions obtained from the addition of deuterium bromide to *trans*-2-butene (40% in deuteriochloroform) displayed the following resonance signals: δ 1.72 (d, J = 6.82 Hz, 3), 1.02 (d, J = 7.0 Hz, 3), 1.8 (m, 1), and 4.12 (m, 1). The nmr spectra of the bromide fractions obtained from the addition of deuterium bromide to *cis*-2-butene (40% in deuteriochloroform) displayed the following resonance signals: δ 1.69 (d, J = 6.73 Hz, 3), 1.02 (d, J = 7.0 Hz, 3), 1.9 (m, 1), and 4.09 (m, 1). Deuterium decoupling of the multiplets in the δ 4.1 region at $^1H\{^2D\}9211.555$ Hz at $-58°$ produced two sets of overlapping double quartets of unequal intensity. The major isomer in the bromide obtained from *trans*-2-butene showed a double quartet at δ 4.12 with $J_{CHDCHBr}$ = 7.88 Hz and $J_{CHDCHBr}$ = 7.15 Hz. The major isomer in the bromide obtained from *cis*-2-butene showed a double quartet at δ 4.09 with $J_{CHDCHBr}$ = 5.16 Hz and J_{CH_3CHBr} = 6.85 Hz. Integration of the outermost peaks of the overlapping double quartets allowed analysis of the bromide mixtures (see following Experimental Section for assignment of the stereochemistry of the 3-deuterio-2-bromobutanes). The results are given in Table III.

The ir spectra of the 3-deuterio-2-butyl acetates obtained from the deuterium bromide catalyzed addition of acetic acid-*O*-*d* to *cis*- and *trans*-2-butene were indistinguishable. The nmr spectra (50% in benzene) of these acetate fractions were also indistinguishable: δ 1.81 (s, 3), 4.82 (m, 1), 1.2–1.6 (m, 1), 1.08 (d, 3, J = 6.6 Hz), and 0.76 (d, 3, J = 7.5 Hz). The acetates were converted to the benzoates for stereochemical analysis using the procedures outlined below. The results are given in Table II.

Procedure A. The 3-deuterio-2-butyl acetate (0.25 g, 2.14 mmol) was added to 2 g of potassium hydroxide dissolved in 7 ml of water. The reaction mixture was refluxed for 3.5 hr, after which time the reaction mixture was cooled and extracted with three 10-ml portions of ether. The ether extract was dried ($MgSO_4$) and concentrated. A mixture of the hydrolysis product, 3 ml of anhydrous pyridine (freshly distilled from potassium hydroxide) and 0.3 ml of benzoyl chloride, was refluxed for 0.5 hr. The reaction mixture was cooled and poured into 10 ml of water in a separatory funnel and extracted with three 10-ml portions of ether. The combined ether extract was dried ($MgSO_4$), concentrated, and distilled in a microstill at 80° (1.4 mm). The infrared spectrum was recorded and the diastereomeric composition determined from the absorbance ratio of the bands appearing at 990 and 972 cm^{-1} and comparison with absorbance ratios derived from mixtures of known diastereomeric composition.[17]

Procedure B. To 0.3 g of lithium aluminum hydride in 20 ml of anhydrous ether in a 50-ml round-bottomed flask equipped with addition funnel, thermometer, and condenser was slowly added 0.5 g (4.27 mmol) of 3-deuterio-2-butyl acetate dissolved in 7 ml of anhydrous ether. The reaction mixture was stirred for 0.5 hr and worked up by slowly adding successively, with stirring, 0.3 ml of saturated aqueous sodium sulfate, 0.3 ml of 20% aqueous sodium hydroxide, and 0.9 ml of water. The precipitate was removed by filtration and the ether extract was dried ($MgSO_4$) and concentrated. The reduction product was converted to the benzoate and analyzed by ir as described above in procedure A.

Determination of the Stereochemistry of the 3-Deuterio-2-bromobutane Derived from *cis*-2-Butene. A mixture of 2.29 g (17 mmol) of 3-deuterio-2-bromobutane (derived from *cis*-2-butene), 3.88 g (17 mmol) of silver benzoate, and 2.45 g (17 mmol) of sodium benzoate in 50 ml of hexamethylphosphoramide was allowed to stir in a stoppered, aluminum foil covered 125-ml erlenmeyer flask in an oil bath at room temperature for 7 days. The reaction mixture was poured over 25 g of ice. After the ice had melted, the reaction mixture was vacuum filtered and the filtrate was extracted with three 20-ml portions of ether. The combined extract was washed with ten 10-ml portions of distilled water. The ether extract was dried ($MgSO_4$), concentrated, and distilled at 80–82° (1.4 mm). The nmr spectrum displayed the following resonance signals: δ 8.1 (m, 2), 7.4 (m, 3), 5.1 (m, 1), and 0.8–2.0 (m, 7). The percentage composition of the erythro and threo isomers was determined by infrared spectroscopy as outlined above[17] showing the presence of 85% erythro benzoate.

Reaction of *trans*-2-Butene with Deuterium Bromide in Acetic Acid-*O*-*d* in the Presence of Lithium Bromide and Lithium Perchlorate. Acetic acid-*O*-*d* (50-ml) containing the desired amount of salt was freeze-degassed and the addition reaction was run as previously described under nonisomerizing conditions. The bromide was isolated and its stereochemical composition determined by nmr in benzene solution as described previously. The results are given in Table II.

Reactions of *cis*- and *trans*-3-Hexene with Deuterium Bromide in Acetic Acid-*O*-*d*. The general procedure described for the reactions of *cis*- and *trans*-2-butene with deuterium bromide in acetic acid was used.

The ir and nmr spectra of the bromide fractions derived from *cis*- and *trans*-3-hexene were indistinguishable. The bromide fractions were converted to the corresponding benzoates using the procedure described above. The deuterium-decoupled nmr spectrum of the benzoate derived from *cis*-3-hexene displayed two overlapping double triplets, the more intense double triplet having $J_{CHDCHBr}$ = 5.8 Hz corresponding to the erythro isomer. The deuterium-decoupled nmr spectrum of the benzoate derived from *trans*-3-hexene displayed two overlapping double triplets, the more intense double triplet having $J_{CHDCHBr}$ = 4.3 Hz. Integration of the deuterium-decoupled spectra allowed the determination of the diastereomeric composition of the benzoate fractions; the benzoate derived from *cis*-3-hexene being 85% erythro and from *trans*-3-hexene 85% threo.

***erythro*-4-Deuterio-3-hexyl Benzoate.** To 20 ml of 0.5 M perdeuterioborane in tetrahydrofuran was added dropwise 1.68 g (20 mmol) of *cis*-3-hexene. The reaction mixture was stirred for 1 hr after which time it was hydrolyzed and oxidized by the addition with stirring of 8 ml of 20% aqueous sodium hydroxide followed by 5 ml of 30% hydrogen peroxide. The reaction mixture was extracted with three 10-ml portions of ether and the ether extract was dried ($MgSO_4$) and concentrated.

In a 25-ml pear-shaped flask was placed 0.93 g (9 mmol) of *erythro*-4-deuterio-3-hexanol, 0.93 g (6.6 mmol) of benzoyl chloride, and 18 ml of anhydrous pyridine (distilled from potassium hydroxide). The mixture was allowed to reflux for 1 hr. After cooling, the reaction mixture was poured into 50 ml of water in a separatory funnel and 25 drops of concentrated sulfuric acid were added. The reaction mixture was then extracted with three 15-ml portions of ether. The ether extract was washed with 200 ml of 2% hydrochloric acid in 25-ml portions, dried ($MgSO_4$), and concentrated, and the residue was distilled at 97–98° (1.5 mm): ir (neat) 2150 (C–D) and 1720 (C=O); nmr ($CDCl_3$) δ 8.05 (m, 2), 7.37 (m, 3), 5.11 (m, 1), and 0.75–1.9 (m, 7). The deuterium-decoupled nmr spectrum displayed a double triplet at δ 5.11 with $J_{CHDCHBr}$ = 5.8 Hz.

Reaction of Cyclopentene with Deuterium Bromide in Acetic Acid-*O*-*d*. Cyclopentene (4.2 g, 61 mmol) was added to 50 ml of 1.22 M deuterium bromide in acetic acid-*O*-*d* and allowed to stand for 20 hr at 25°. A 1-ml aliquot was removed and added to an excess of *N*,*N*-dimethylaniline. The bromide–acetate ratio was determined by glpc analysis on a 10-ft 15% Carbowax on Haloport F column at 100°.

The remainder of the reaction mixture was poured into 100 ml of water and was extracted with five 20-ml portions of ether. The combined ether extract was washed with saturated aqueous sodium bicarbonate until the evolution of carbon dioxide ceased. The organic layer was dried ($MgSO_4$) and concentrated. The cyclopentyl bromide and acetate fractions were isolated by preparative glpc using a 10-ft 20% Carbowax 20M on Chromosorb W column at 100°.

The cis–trans composition of the bromide fractions was determined from the absorbance ratio of the bands at 1350 and 1250 cm^{-1} and comparison with the absorbance ratios derived from known mixtures of *cis*- and *trans*-2-deuteriocyclopentyl bromide. The results are given in Table III.

The cis–trans composition of the cyclopentyl acetate fractions was determined after conversion to the corresponding benzoates according to the following procedure. To 0.3 g (7.2 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether in a 50-ml round-bottomed, three-necked flask equipped with an addition funnel, thermometer, and condenser, was added dropwise 0.5 g (3.9 mmol) of 2-deuteriocyclopentyl acetate dissolved in 7 ml of anhydrous ether. The temperature was maintained below 0° and the reaction mixture was stirred for 0.5 hr. The reaction mixture was hydrolyzed by the addition of 0.3 ml of saturated aqueous sodium sulfate, 0.3 ml of 15% sodium hydroxide and 1.0 of water. The precipitate of inorganic salts was removed by filtration and the ether layer was dried ($MgSO_4$) and concentrated.

A mixture of 0.25 g (2.9 mmol) of the cyclopentanol and 0.5 g (2.9 mmol) of recrystallized *p*-nitrobenzoyl chloride was heated in a test tube for 1 min. Water was then added and the oil produced

was crystallized by cooling to −15°. The solid was recovered by filtration and was recrystallized from Skelly-Solve B; mp 55–57°. The cis–trans composition of the 2-deuteriocyclopentyl *p*-nitrobenzoate was determined by infrared spectroscopy from the absorbance ratio of the peaks appearing at 1159 and 1173 cm^{-1} by comparison with absorbance ratios derived from mixtures of known cis–trans composition. The results are given in Table III.

***trans*-2-Deuteriocyclopentyl Bromide.** A solution of perdeuterioborane in tetrahydrofuran (10 ml of a 0.567 *M* solution, 5.7 mmol) was added dropwise to 1.2 g (17.1 mmol) of cyclopentene contained in a three-necked, round-bottomed flask. The reaction mixture was stirred for 0.5 hr after which time it was hydrolyzed and oxidized with 2 ml of 1 *N* sodium hydroxide and 1 ml of 30% hydrogen peroxide. The product was isolated by extraction with three 10-ml portions of ether. The combined ether extract was dried ($MgSO_4$) and concentrated.

To a cooled (ice bath) solution of 5.15 g (19 mmol) of phosphorus tribromide in 20 ml of methylene chloride, was added slowly, with stirring, 2.56 g (16 mmol) of bromine dissolved in 15 ml of methylene chloride. To this mixture was added 1.10 g (11 mmol) of *cis*-2-deuteriocyclopentanol dissolved in 10 ml of methylene chloride. The reaction mixture was stirred for 3 hr, after which time 50 g of ice–water was added and the stirring continued for another hour. The organic and aqueous layers were separated and the organic phase was removed and washed successively with water, 5% aqueous sodium bicarbonate, and saturated aqueous sodium chloride and was dried ($MgSO_4$) and concentrated. The *trans*-2-deuteriocyclopentyl bromide was purified by preparative glpc on a 5-ft 20% Carbowax 20M on Chromosorb W column at 125°.

***cis*-2-Deuteriocyclopentyl Bromide.** In a three-necked, round-bottomed 1000-ml flask, equipped with a condenser and addition funnel, was placed a solution of 65.3 g (0.322 mol) of *m*-chloroperbenzoic acid dissolved in 500 ml of anhydrous dioxane (distilled from sodium). The contents of the flask was cooled in an ice–water bath and 21.9 g (0.322 mol) of cyclopentene was added dropwise. The reaction mixture was allowed to stand in the ice–water bath for 1 hr, after which time the flask was stoppered and placed in the freezer overnight. The reaction mixture was directly distilled, the fraction up to 100° being collected. The cyclopentene oxide was purified by distillation through a 12-in. glass-helices packed column.

To a solution of 1.14 g (27.2 mmol) of lithium aluminum deuteride in 50 ml of anhydrous ethyl ether contained in a 100-ml round-bottomed, three-necked flask equipped with a dropping funnel, reflux condenser, drying tube and magnetic stirrer, was added a solution of 1.76 g (21 mmol) of cyclopentene oxide dissolved in 10 ml of anhydrous ether. The ice bath was removed and the reaction mixture was allowed to warm to room temperature and was stirred for 3 hr and finally refluxed for 1 hr. The reaction mixture was cooled to 0° and hydrolyzed by the cautious addition of 4.6 ml of 10 *N* sulfuric acid. The reaction mixture was poured into 100 ml of distilled water and was extracted with five 5-ml portions of ether. The combined ether extract was washed with 100 ml of saturated aqueous sodium chloride, dried ($MgSO_4$), and concentrated.

cis-2-Deuteriocyclopentyl bromide was prepared from *trans*-2-deuteriocyclopentanol by the method described for the preparation of *trans*-2-deuteriocyclopentyl bromide from *cis*-2-deuteriocyclopentanol and was purified by preparative glpc.

***cis*- and *trans*-2-Deuteriocyclopentyl *p*-Nitrobenzoate.** A mixture of 0.3 g (3.6 mmol) of *cis*- or *trans*-2-deuteriocyclopentanol and 0.66 g (3.9 mmol) of *p*-nitrobenzoyl chloride was heated gently in a 10-ml pear-shaped flask for 10 min. The solid product was dissolved in 20 ml of ether and was washed with 10 ml of 5% aqueous sodium bicarbonate and with two 10-ml portions of distilled water. The ether was evaporated and the solid was recrystallized from Skelly-Solve B, mp 56.5–57°.

Kinetic and Product Ratio Studies. The desired amount of olefin was brought to 5.0 ml with acetic acid and added to 50.0 ml of standardized hydrogen bromide in acetic acid and maintained at 25.0 ± 0.2°. Aliquots (0.5 ml) were periodically withdrawn by syringe and quenched in a known excess of standard sodium acetate in acetic acid. The excess sodium acetate was back titrated potentiometrically with standardized *p*-toluenesulfonic acid in acetic acid.

Aliquots (0.5 ml) were also periodically removed and quenched in 0.5 ml of *N*,*N*-dimethylaniline. The quenched reaction mixture was directly analyzed by glpc using a 5-ft 10% Carbowax 20M on Chromosorb W column at 110°. The bromide to acetate ratio was determined by integration of the peak areas and corrected for response ratios.

Acidity Function Determination. A 2.0×10^{-3} *M* stock solution of 4-chloro-2-nitroaniline in freshly prepared anhydrous acetic acid was prepared by dissolving 0.0346 g of the amine in 100.0 ml of acetic acid. Aliquots (1 ml) of this stock solution were placed in 10-ml volumetric flasks and measured amounts of 1.54 *M* hydrogen bromide in acetic acid were added to each of the volumetric flasks followed by dilution to 10 ml with acetic acid. The molarity of hydrogen bromide varied from 0.05 to 0.80 *M*. The ultraviolet spectra of the solutions were recorded on a Cary 15 ultraviolet spectrophotometer using solutions of the same concentration of hydrogen bromide in acetic acid as the reference sample. The absorbance was determined at 410, 430, and 445 nm and the concentration of unprotonated amine was calculated. The H_0 was calculated using the equation

$$H_0 = pK_{BH^+} - \log [(BH^+)/(B)]$$

using a value of −1.03[39] for pK_{BH^+}. The H_0 data were plotted *vs.* hydrogen bromide concentration and an average curve was constructed from the data from the three different wavelengths. The average curve was curve fitted producing the following function from log [hydrogen bromide] = −1.3 to 0.0.

$$-H_0 = 1.275 + 0.648(-1.3 - \log (HBr)) - 0.24(-1.3 - \log (HBr))^2 + 0.02(-1.3 - \log (HBr))^3 - 0.035(-1.3 - \log (HBr))^4$$

(39) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).