Table VII. Nmr Shifts of p-X-Phenyldimethylcarbinols[a]

X	Aromatic	Me	X	Bp, °C (mm)
H	7.25 (m)[c]	1.43	...	51 (1)
CH_3	7.25, 6.95	1.45	2.28	48 (0.3)
OCH_3	7.25, 6.68	1.43	3.68	80 (0.03)
CF_3[b]	7.55	1.52	ϕ +63.21	57 (0.9)

[a] CCl_4. [b] Mp 42°. [c] m = multiplet.

Table VIII. Nmr Shifts of p-X-Phenyldimethylcarbinyl Chlorides[a]

X	Aromatic	Me	X
H	7.40 (m)[b]	1.97	...
CH_3	7.38, 7.07	1.92	2.31
OCH_3	7.40, 6.75	1.95	3.75
CF_3	7.68	1.99	ϕ +63.63

[a] CCl_4. [b] m = multiplet.

phenone. The nmr spectra and boiling points are listed in Table VII.

p-X-Phenyldimethylcarbinyl chlorides[26] were prepared by reaction of the appropriate carbinol with HCl at 0° (H, CH_3, OCH_3) or with Lucas reagent (CF_3) at 20°. Their nmr spectra are listed in Table VIII.

2,3-Dimethyl-2-chlorobutane was prepared by chlorination of tetramethylethylene with anhydrous HCl at 0° in CH_2Cl_2; nmr (CCl_4) septuplet (J = 6.3 Hz) δ 1.88 (1), singlet 1.51 (6), and doublet (J = 6.3 Hz) 1.05 (6).

1-p-CF_3-Phenyl-1-t-butylethylene. Five grams of p-CF_3-phenyl-t-butylmethylcarbinol was stirred overnight with a mixture of 50 ml of ether and 50 ml of thionyl chloride. Evaporation of the solvent and excess thionyl chloride yielded a foul-smelling residue which had no hydroxyl in the ir and nmr chemical shifts which were very similar to those of the starting alcohol. Distillation at 2.5 mm yielded the title compound, bp 75° (7 mm); nmr (CCl_4) δ 7.52 (2), 7.22 (2), 5.21 (1), 4.76 (1), and 1.12 (9); ^{19}F ϕ 63.16.

Anal. Calcd for $C_{13}H_{18}$: C, 82.05; H, 9.53. Found: C, 81.80; H, 9.35.

2,3,3-Trimethyl-2-chlorobutane was obtained from Aldrich.

Nmr spectra were obtained on Varian Associates Model HA 100 (^1H) and A56-60A (^{19}F) nmr spectrometers. Unless otherwise indicated, all proton shifts are in SO_2 solvent from external (capillary) TMS. Shifts in CCl_4 (internal TMS) may be converted to SO_2 (external TMS) by an upfield shift of 0.25 ppm. For the compounds in this paper, the maximum error in this procedure is δ 0.03. ^{19}F shifts are from CCl_3F in a separate tube (ions) or from internal CCl_3F as solvent (covalent precursors).

Preparation of the Ions. SbF_5 (0.075 ml) was dissolved in 0.5 ml of SO_2 at −10°. The solution was then cooled to −78° causing most of the SbF_5 to precipitate out of solution. The organic chloride (50 mg) was then carefully added to the surface of the SO_2 solution. After standing for 3 min to allow the organic precursor to cool to −78°, the solution was then stirred at −78° until the insolubles dissolved. Generally 5 min was required for the benzylic chlorides and 15–20 min for the tertiary chlorides. As the ion is quite soluble in SO_2 at this temperature, but SbF_5 and organic chlorides are almost insoluble, ionization proceeds at a moderate rate.

Quenching experiments with methanol were carried out as described previously.[6] In preparative scale runs with analysis by nmr the yields were over 75%.

Acknowledgment. Support of the work by grants of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged. Texaco, Inc., is thanked for a graduate fellowship (M. B. C.). Professor H. C. Brown is thanked for critical discussions.

Polar Additions to the Styrene and 2-Butene Systems.[1] I. Distribution and Stereochemistry of Bromination Products in Acetic Acid

John H. Rolston[2] **and Keith Yates**

Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada. *Received October 5, 1968*

Abstract: The products of bromine addition in acetic acid have been investigated for a series of ten ring- and side-chain-substituted styrenes and for *cis*- and *trans*-2-butenes. The styrenes generally give substantial amounts of acetoxy bromides as well as the expected 1,2-dibromides, but the butenes give almost exclusively dibromide under the same conditions. The acetoxy bromides isolated are shown to be the 1-acetoxy-2-bromo derivatives, with one exception. The additions to the styrenes are nonstereospecific, although *trans* addition is favored, whereas additions to *cis*- and *trans*-2-butenes are completely stereospecific and *trans*. Acetoxy bromide formation was found to be more stereoselective than dibromide formation. The results are taken as evidence that the intermediates formed in the styrene reactions resemble open α-phenylcarbonium ions more than bromonium ions.

It is widely accepted that the electrophilic addition of bromine to olefins in polar solvents proceeds stereospecifically and *trans*. Further, it is generally held that this stereospecificity results from the formation of cyclic bromonium ion intermediates of the type originally postulated by Roberts and Kimball.[3] However despite their long-standing acceptance the evidence on which these intermediates is based can hardly be considered

---

(1) Presented in part at the 50th Canadian Chemical Conference, Toronto, June 1967.

(2) Department of Chemistry, King's College, University of London, London.

(3) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

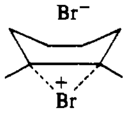
Table I. Selected Nmr Data on Styrene Derivatives

Compound	Approximate proton chemical shifts[a] α-Protons	β-Protons	Acetoxy
$C_6H_5\underset{X}{CH}\underset{Y}{CH_2}$			
X = Br, Y = Br	5.08 5.053[b]	4.00, 3.97 4.013, 3.949[b]	
X = OAc, Y = Br	5.91[c]	3.46, 3.56	1.97
X = OH, Y = Br	4.75[c]	3.32, 3.42	
X = OAc, Y = H	5.78	1.48	1.95
X = H, Y = OAc	2.93	4.30	2.02
$m\text{-}ClC_6H_4\underset{X}{CH}\underset{Y}{CH_2}$			
X = Br, Y = Br	5.02	3.92, 3.90	
X = OAc, Y = Br	5.92	3.45, 3.56	2.02
$m\text{-}NO_2C_6H_4\underset{X}{CH}\underset{Y}{CH_2}$			
X = Br, Y = Br	5.20	4.06, 3.97	
X = OAc, Y = Br	6.03	3.70, 3.60	2.15

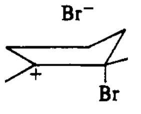
[a] In parts per million (ppm) from internal TMS in CCl_4. [b] From detailed spectral analysis in E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1155 (1966). [c] Similar to ABX pattern iii in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution N.M.R. Spectroscopy," Vol. I., Pergamon Press, New York, N. Y., 1965, p 364.

conclusive. It is still largely true as Gould[4] pointed out several years ago that "few organic reaction mechanisms have been accepted so widely while supported with such limited data."

Although many examples of 1,2-*trans* additions of bromine to olefins are known, these are largely confined to cyclic double bond systems, where *trans*-diaxial addition appears to be firmly established.[5-7] However, in these systems the same mode of addition would be expected from either a bromonium ion (I) or a bromocarbonium ion (II) intermediate because of the bulk of the first attached bromine and the lack of free rotation of the C_α–C_β bond in the cyclic system, provided that reorientation of the ions in II is faster than ion pair collapse from the *cis* side, as seems reasonable.



I



II

For acyclic double bond systems the evidence for stereospecific *trans* addition in polar solvents is limited to the results on the bromination of maleic and fumaric acids[8] which originally led Roberts and Kimball to postulate the bromonium ion intermediate and some limited results on *cis*- and *trans*-2-butenes.[9] However in neither case was the *trans* product shown to be formed exclusively, and more recently Bell[10a] has shown that whereas the diethyl ester of fumaric acids adds bromine *trans*, as expected, the diethyl ester of maleic acid gives predominantly *cis* addition under the same conditions. Also, the stereospecificity of bromine addition to *cis*- and *trans*-stilbenes has been shown to depend markedly on solvent polarity.[10b]

A further difficulty is that bromonium ion intermediates are predicated largely on stereochemical grounds, which involves the assumption that free rotation in open bromocarbonium ions is much more rapid than collapse of solvent-separated ion pairs, and thus would lead to loss of stereospecificity. This has never been established, and in fact there is some evidence[11] that these rates of rotation are not as rapid as supposed. On the other hand the elegant nmr studies of Olah and Bollinger[12a] have shown clearly that cyclic halonium ions can and do exist in solvents of extremely low nucleophilicity, particularly for simple aliphatic systems. However, this does not establish that they are present as intermediates in halogenation reactions. The role of anchimeric assistance by neighboring bromine in certain reactions[12b] is well recognized and provides further evidence for bromonium ion participation, but again does not establish that they are intermediates in halogen addition reactions.

Nonetheless, increasing evidence[10,13-16] that electrophilic additions to the double bond are not typically stereospecific and *trans* makes it obvious that considerably more systematic work is needed before the mech-

---

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N.Y., 1959, p 523.

(5) S. Winstein, *J. Am. Chem. Soc.*, **64**, 2792 (1942).

(6) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950); D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951); G. H. Alt and D. H. R. Barton, *ibid.*, 4284 (1954).

(7) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).

(8) A. McKenzie, *J. Chem. Soc.*, 1196 (1912); K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64**, 679 (1942).

(9) W. G. Young, R. T. Dillon, and H. J. Lucas, *ibid.*, **51**, 2528 (1929); R. T. Dillion, W. G. Young, and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

(10) (a) R. P. Bell and M. Pring, *J. Chem. Soc., B*, 119 (1966); (b) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962); J. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

(11) B. Benjamin, H. J. Schaefer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

(12) (a) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); (b) S. Winstein and H. J. Lucas, *ibid.*, **61**, 2845 (1939).

(13) R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965).

(14) R. C. Fahey and H.-J. Schneider, *ibid.*, **90**, 4429 (1968).

(15) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(16) G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

Table II. Selected Nmr Data on β,β-Dimethylstyrene Derivatives

Compound	Proton chemical shifts[a] α-Hydrogen	β-Methyl	Phenyl	Acetoxy
$\underset{X}{C_6H_5CH}\underset{Y}{C}(CH_3)_2$				
X = Br, Y = Br	5.21	1.85, 1.98	7.1–7.6	
X = OAc, Y = Br (A)	5.85	1.68	7.2–7.5	2.05
X = Br, Y = OAc (B)	5.58	1.51	6.1–7.5	1.90
X = OAc, Y = OH (C)	5.57	1.11	7.3	2.05
X = Br, Y = OH	4.89	1.24, 1.30	7.1–7.5	

[a] In parts per million (ppm) from internal TMS in CCl_4.

Table III. Selected Nmr Data of β-Methylstyrene Derivatives

Compound	Proton chemical shifts[a] α-Protons	β-Methyl	Acetoxy
$\underset{X}{C_6H_5CH}\underset{Y}{CH}CH_3$			
erythro X = Br, Y = Br	4.95 (10.5)[b]	2.00 (6.0)[c]	
threo X = Br, Y = Br	5.15 (5.5)	1.60 (6.5)	
"*erythro*" X = OAc, Y = Br	5.92 (5.5)	1.55 (7.0)	1.99
"*threo*" X = OAc, Y = Br	5.79 (8.0)	1.45 (7.0)	2.00
"*erythro*" X = OH, Y = Br	4.90 (3.0)	1.47 (7.0)	
erythro X = Cl, Y = Cl[d]	4.80 (8.0)	1.68 (6.4)	
threo X = Cl, Y = Cl[d]	4.92 (5.7)	1.41 (6.6)	
"*erythro*" X = OAc, Y = Cl[d]	5.81 (5.4)	1.43 (6.5)	2.08
"*threo*" X = OAc, Y = Cl[d]	5.69 (7.3)	1.30 (6.6)	2.05

[a] In parts per million (ppm) from internal TMS in CCl_4. [b] Vicinal coupling constant. [c] Coupling constant with β-proton. [d] Taken from ref 13.

anisms of such reactions are clearly understood. The current resurgence of interest in electrophilic additions generally attests to this.

We have therefore investigated the product distribution, stereochemistry, and kinetics of a number of ring- and side-chain-substituted styrenes both as a function of reaction conditions and substrate structure. Similar studies on *cis*- and *trans*-2-butenes have been carried out for comparison purposes. The present paper deals with the distribution and stereochemistry of the reaction products in acetic acid.

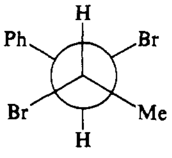
Results and Discussion

Identification of Products. The predominant product from the addition of bromine in acetic acid to ten substituted styrenes and two butenes is the expected dibromide. However, significant amounts of acetoxybromides were also formed in most cases. The single bromoacetate isolated from bromine addition to styrene was shown to be 2-bromo-1-phenylethyl acetate by comparison of its nmr spectra and glpc retention times with those of an authentic sample prepared by acetylation of 2-bromo-1-phenylethyl alcohol. The chemical shift (5.91 ppm) of the methine proton, α to the acetoxyl group, in this acetoxy bromide is similar to that in 1-phenylethyl acetate (5.8 ppm) and clearly different from either of the methylene signals (2.90 and 4.30 ppm) in 2-phenylethyl acetate. The major features of the nmr spectra of the products from styrene and 3-chloro- and 3-nitrostyrenes are given in Table I.

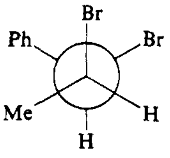
Comparison with the spectra of the products from styrene itself shows that these substituted styrenes also form 2-bromo-1-phenylethyl acetates. The acetoxybromo adduct from α-methylstyrene was also shown to be the 1-acetoxy-2-bromo derivative by hydrolyzing the isolated dibromo adduct to the bromohydrin, followed by acetylation to give an identical acetoxy bromide. The position of the OH group in this bromohydrin was shown to be α to phenyl by reduction with $LiAlH_4$ to give α,α-dimethylbenzyl alcohol.

In addition to the dibromide, the crude bromination product from β,β-dimethylstyrene contained two products, A and B, as shown by two signals at 5.85 and 5.58 ppm in the nmr spectrum. Chromatography of the crude mixtures gave two components, A and C, after initial elution of the dibromide. Both contained acetoxyl groups but comparison of the nmr spectra of these pure components with that of the crude reaction mixture showed that A was present but that C was not present in the original products. Compound C which also contained a hydroxyl group appeared to be derived from B. The structures of A and B were assigned on the basis of combustion analysis and nmr spectral comparisons (Tables I and II) as 1-acetoxy-2-bromo-2-methyl-1-phenylpropane and 1-bromo-2-acetoxy-2-methyl-1-phenylpropane, respectively. An authentic sample of the latter was prepared and its nmr spectrum was found to be identical with that of compound B. It was also found that chromatography on Florisil converted this acetoxy bromide into a hydroxy acetate indistinguishable from compound C.

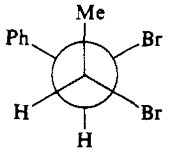
Addition of bromine to *cis*- or *trans*-β-methylstyrene (1-phenylpropene) gave a mixture of diastereomeric dibromides. Both have been previously reported,[17] the *erythro* compound being a white solid and the *threo* isomer a liquid at room temperature. A pure sample of the *erythro* isomer was obtained by recrystallizing the major product of bromine addition to *trans*-β-methylstyrene in CCl_4 at −60°. Similar treatment of *cis*-β-methylstyrene gave a *threo* product containing about 15% *erythro* impurity. However the major features of its nmr spectrum could easily be deduced from the crude product and those of the pure *erythro* compound. These are given in Table III.



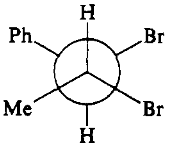
III



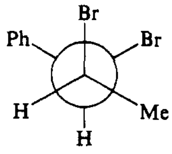
IV



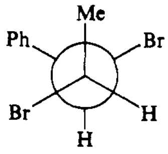
V



VI



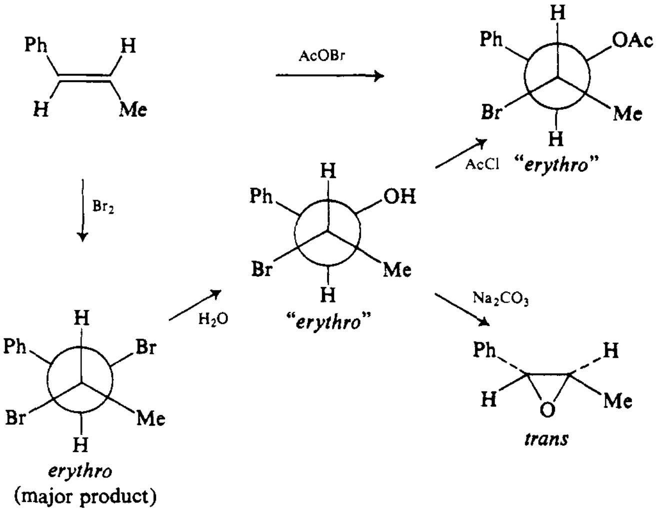
VII



VIII

The nmr spectra of the two diastereomers can be shown to be in agreement with the assigned stereochemistry from a consideration of the possible conformational isomers. The three main conformations of the *erythro* compound are shown in the Newman projection below. Consideration of both electrostatic interactions and the steric requirements of the Br, CH_3, and Ph groups leaves little doubt that III is of lowest energy, and will predominate over the other two. Since this conformer has two protons in an *anti* relationship the coupling constant J_{AB} is expected on the basis of Karplus relationship[18] to be about 9 cps. The exact magnitude of J_{AB} however depends on the remaining substituents and a value of about 11 cps is to be expected for dibromides[19] and dichlorides[20] when the dihedral angle is 180°. The *J* values for *gauche* protons on the other hand are expected to be much lower at about 3 cps. In the *threo* dibromide, where it is no longer clear which conformation is most stable, no one conformer is expected to predominate. If, as seems reasonable, substantial populations of all three conformers are present, the observed value of J_{AB} for the *threo* compound should be somewhere near the average for VI, VII, and VIII and probably in the range 5–7 cps, well below that expected for the *erythro* isomer. The observed coupling constants are 10.5 and 5.5 cps for the solid and liquid diastereomers, respectively, in agreement with the assigned stereochemistry. The chemical shifts of the β-methyl protons in the *erythro* and *threo* dibromides are also characteristic of the stereochemistry. The β-methyl resonance of the *erythro* dibromide is a doublet (J = 6.0 cps) at 2.00, while that of the *threo* is a doublet (J = 6.5 cps) at higher field (1.60). These results parallel those reported for the dichlorides.[13] Thus the proximity of the β-methyl to phenyl in VI and VIII of the *threo* isomer results in an upfield shift relative to the *erythro* where the predominant conformer is III.

The two acetoxy bromides obtained from the *cis*- and *trans*-β-methylstyrenes, respectively, were initially assigned to be the diastereomeric 1-acetoxy-2-bromo derivatives from the chemical shifts of the α-protons at 5.92 and 5.79, respectively (see earlier discussion). Although the terms "*erythro*" and "*threo*" are not strictly applicable here, they will be used so that the stereochemistry of acetoxy bromide formation can be related directly to that of dibromide formation. The stereochemistry of the acetoxy bromides can not be assigned unambiguously from nmr spectra since the coupling constants (see Table III) do not fall clearly into two ranges as found for the dibromides, nor are the predominant conformations as easy to assign. However, the chemical shifts of the β-methyl groups indicated that the major acetoxy bromo product from the *cis* olefin was the "*threo*" since its signal occurred at higher field (δ 1.45) than that from the *trans* olefin (δ 1.55). Final assignment was made on the basis of the following chemical transformations. An authentic sample of *erythro*-2,3-dibromo-1-phenylpropane was solvolyzed to give the "*erythro*"-(±)-1-hydroxy-2-bromo-1-phenylpropane by the method of Fischer.[21] This was converted to an epoxide with a vicinal coupling constant (J = 1.8 cps) consistent with a *trans* epoxide. A further sample of the above "*erythro*" bromohydrin was acetylated to give an "*erythro*"-1-acetoxy-2-bromo-1-phenylpropane identical with that prepared by acetyl hypobromite addition to *trans*-β-methylstyrene. These transformations are summarized below and confirm the tentative nmr assignments.



Bromine additions to *cis*- and *trans*-2-phenyl-2-butenes in each case give predominantly a mixture of diastereomeric dibromides. The result of *trans* addition to *cis*-2-phenyl-2-butene would be *threo*-2,3-dibromo-2-phenylbutane (IX, R = CH_3) which is structurally related to the *trans*-addition product from *trans*-β-

---

[17] W. R. R. Park and G. F. Wright, *J. Org. Chem.*, **19**, 1435 (1954).

[18] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[19] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (London), **A252**, 506 (1959); R. O. C. Norman and C. B. Thomas, *J. Chem. Soc., B*, 598 (1967).

[20] P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *ibid.*, 827 (1966); M. C. Calabeiro and M. D. Johnson, *ibid.*, 565 (1967).

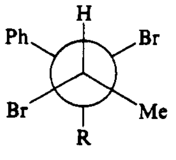
[21] F. Fischer, *Chem. Ber.*, **90**, 357 (1957).

Table IV. Product Distribution from Bromine Additions in Acetic Acid

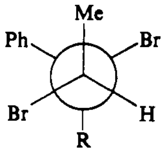
Olefin	Addition procedure	Product,[a] % 1,2-Dibromo	1-Acetoxy-2-bromo	2-Acetoxy-1-bromo
Styrene	i	67.6	32.4	0
	ii	79.8	20.2	0
3-Chloro	i	71.5	28.5	0
	ii	77.4	22.6	0
3-Nitro	i	86.8	13.2	0
α-Methyl	i	86.4	13.6	0
	ii	98.0	2.0	0
cis-β-Methyl	ii	80.4	19.6[b]	0
	iii	79.3	20.7[b]	0
trans-β-Methyl	ii	76.6	23.4[c]	0
	iii	78.2	21.8[c]	0
β,β-Dimethyl	ii	79.0	15.7	5.3
			Total acetoxy bromide[d]	
cis-α,β-Dimethyl	ii	82	18[e]	
	iii	81	19[e]	
trans-α,β-Dimethyl	ii	88	12[e]	
	iii	84	16[e]	
α,β,β-Trimethyl	ii	96	4	
cis-2-Butene	ii	98	2	
trans-2-Butene	ii	98	2	

[a] Percentage of total recovered products determined by nmr analysis. Total yields were 83–91% of theoretical. [b] At least 95% "*threo*." [c] At least 95% "*erythro*." [d] Structures of acetoxy bromides not investigated. [e] Includes some bromohydrin formed by hydrolysis during work-up.

methylstyrene, namely *erythro*-1,2-dibromo-1-phenylpropane (IX, R = H). Similarly the *erythro*-2,3-dibromo-2-phenylbutane (X, R = CH_3) is related stereochemically to the *threo*-1,2-dibromo-1-phenylpropane (X, R = H). Since in every pair of diastereomers in Table III the *erythro* form has its β-methyl resonance at lower field than the *threo* it should be possible to assign the stereochemistry of the related dibromides from *cis*- and *trans*-2-phenyl-2-butenes. The major dibromide from the *cis* olefin has its β-methyl signal at δ 1.96 while that of the major dibromide from the *trans* olefin is at 1.56. Therefore assuming that changing an α substituent from H to CH_3 does not grossly change[22] the relative stabilities of the various conformations, these dibromides are the *threo*- and *erythro*-2,3-dibromo-2-phenylbutanes, respectively. The structure of the minor acetoxy bromide products formed from these olefins was not investigated.



IX



X

Product Distribution. The products obtained from addition of bromine to each of the twelve olefins investigated are shown in Table IV. Although as expected the dibromide is the major product in all cases, substantial amounts of solvent-incorporated products are also found, particularly from the styrenes. These generally give about 15–30% acetoxy bromide, in sharp contrast to the 2-butenes which yield virtually exclusively the dibromo adduct. It is also interesting that these acetoxy bromides are formed in a highly regiospecific manner[23] (*i.e.*, Markovnikov), being with one exception the 1-acetoxy-2-bromo adducts. Both these results suggest that the reaction intermediates from the styrenes possess considerable free carbonium ion character at the α-carbon. Any strong bromine bridging, such as in a bromonium ion, would disperse the cationic charge in the intermediate onto both carbons as well as bromine. This would reduce the susceptibility to attack at either carbon by the weakly nucleophilic solvent and also lead to nonregiospecific products. The fact that only β,β-dimethylstyrene gives both possible acetoxy bromides could be attributed in this case either to bromine bridging to the α-carbon or to a competition between a benzyl and a *t*-butyl-type carbonium ion intermediate of similar stability.

If the intermediates from the styrenes generally resemble α-phenylcarbonium ions this could also explain why the lowest yields of solvent-incorporated product are obtained from the α-methyl-substituted styrenes, where the steric effect of an α-methyl group would hinder the approach of solvent to the carbonium ion center.

Product Stereochemistry. More interesting are the stereochemical results shown in Table V. The results from both the β-methylstyrenes and 2-phenyl-2-butenes show that bromine addition to the styrene system is clearly not a stereospecific process. Although the additions are predominantly *trans* in this solvent, variable stereoselectivity is shown, with *trans*/*cis* ratios ranging from 1.7 to 4.9.[24] These results again contrast sharply with those obtained from additions to *cis*- and *trans*-2-butenes, both of which are completely stereospecific and

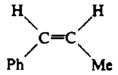
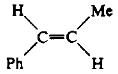
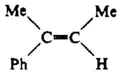
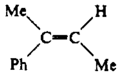
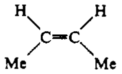
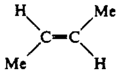
---

(22) C. A. Kingsbury and W. B. Thorton, *J. Org. Chem.*, **31**, 1000 (1966).

(23) A. Hassner and F. Boerwinkle, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, Abstract P-81.

(24) Some of these stereochemical results parallel those recently obtained by Fahey and Schneider.[14]

Table V. Stereochemistry of Dibromo Adducts

Olefin	Addition procedure	% *erythro*[a] Nmr[b]	% *erythro*[a] Glpc[c]	% *threo*[a] Nmr	% *threo*[a] Glpc	% *trans* addition
	ii	27.9	26.3	72.1	73.7	73
	iii	17.4	16.7	82.6	83.3	83
	ii	83.3	82.9	16.7	17.1	83
	iii	82.8	83.4	17.2	16.6	83
	ii	31.9		68.1		68
	iii	33.0		67.0		67
	ii	62.9		37.1		63
	iii	62.5		37.5		62
	ii	0	0.5	100	99.5	100
	iii	0		100		100
	ii	100	99.5	0	0.5	100
	iii	100		0		100

[a] Based on total dibromide. [b] Analysis based on integrated intensities of β-methyl signals. [c] Analysis based on calibrated peak areas.

trans. This again strongly indicates that the intermediates from the styrene systems resemble free α-phenylcarbonium ions, in which any neighboring bromine interaction is weak, more than they resemble bromonium ions of the Roberts and Kimball type.[3] On the other hand, the results from the 2-butene system, where there is no α-phenyl group present to assist in charge dispersal, are more consistent with strong bromine bridging in the intermediate.

The stereochemistry of acetoxy bromide formation from *cis*- and *trans*-β-methylstyrenes does not however parallel that shown in Table V for the dibromides. The *cis* olefin gives almost exclusively "*threo*"-1-acetoxy-2-bromo-1-phenylpropane, while the *trans* olefin gives almost exclusively the "*erythro*" diastereomer. This shows that solvent attack on the intermediate takes place almost entirely from the *trans* side.[13] This can be explained by initial formation of an intimate ion pair, in which immediate collapse to give dibromide cannot easily occur because of the bulk of the first attached bromine atom. Dibromide formation can occur more easily when Br^- counterion has reoriented itself (presumably through a solvent-separated ion pair) to the opposite side of the cation. This can take place with or without net rotation of the C_α–C_β bond to give both *cis*- and *trans*-addition products. On the other hand favorably oriented solvent molecules are always in a position to attack easily from the opposite side to the incoming bromine, leading to predominantly *trans*-acetoxy bromide formation.

Product Dependence on Addition Procedure. It can be seen from Tables IV and V that the method of addition of bromine has some influence on both product distribution and stereochemistry. Procedure i, in which bromine is present in relatively high local concentrations, consistently gave higher yields of acetoxy bromide. Since under these conditions products are undoubtedly being formed by both kinetically simple first-order processes (in bromine) as well as the more complicated second-order process[25] it was decided to use procedure ii as a general method so that both products and kinetics could be studied under as nearly identical conditions as possible. Using this method of addition the standing concentration of bromine is kept below 10^{-3} *M* so that the products isolated are formed essentially by the kinetically simple first-order bromine and first-order olefin process. Procedure iii was used deliberately in some cases to investigate the possibility that the *cis*-addition products observed result from preliminary isomerization of unreacted olefin by the HBr generated during the reaction, followed by *trans* addition. This is clearly not the case, as shown by the results in Table V. The stereochemical results in five out of six cases studied are not changed by this procedure, and even in the case of *cis*-β-methylstyrene, where there is the largest driving force for olefin isomerization, there is only a modest increase in the percentage of *trans* addition, showing that isomerization of starting olefin is not extensive even under these extreme conditions.

Experimental Section

All infrared spectra (CCl_4) were recorded on a Perkin-Elmer Model 137B instrument. All nmr spectra (CCl_4) were obtained with a Varian Model A-60 spectrometer. Peak positions are given in parts per million (ppm) relative to TMS ($\delta = 0$). Gas–liquid partition chromatography was carried out on a Varian Aerograph Model A-705 Autoprep instrument using commercial columns. Melting points and boiling points are uncorrected. Microanalyses were performed by A. B. Gygli Microanalysis Laboratory, Toronto.

Materials. Styrene, *m*-chlorostyrene, *m*-nitrostyrene, and 2-phenylpropene (α-methylstyrene) were obtained commercially (Columbia or Aldrich) and were fractionally distilled under reduced pressure in a Schweizer still (Nester-Faust) equipped with a 25-cm Vigreux column. Fractions were checked by glpc and redistilled if necessary.

cis-1-Phenylpropene (*cis*-β-methylstyrene) was prepared by catalytic hydrogenation of 1-phenylpropyne.[26] 1-Phenylpropene was

---

(25) K. Yates and W. V. Wright, *Can. J. Chem.*, **45**, 167 (1967).

(26) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3465 (1963).

purchased from Columbia Chemicals and contained about 90% *trans* isomer. Purer samples of the *cis* (bp 160° (760 mm)) and *trans* (bp 98° (84 mm)) isomers were then obtained by distillation through a spinning-band column. Suitable fractions were purified immediately before use by preparative glpc using a 20 ft × $\frac{3}{8}$ in. column of 30% SE-30 on Chromosorb W at 170°. Final samples of *cis*- and *trans*-1-phenylpropenes were at least 99.9% pure. 2-Methyl-1-phenylpropene (β,β-dimethylstyrene) was prepared by dehydration of benzyldimethylcarbinol, bp 108–112° (21 mm) (lit.[27] bp 104–105° (17 mm)), which had been obtained in 85% yield by the addition of benzylmagnesium chloride to acetone. A mixture of 21 g of carbinol and 100 ml of 85% H_3PO_4 was heated under a pressure of 20 mm and the distillate collected up to 50 °. The crude olefin (75% yield) was dried and distilled through a spinning-band column (bp 134–135° (195 mm)). Fractions were checked by glpc and purified by preparative glpc where necessary. *cis*- and *trans*-2-Phenyl-2-butenes were prepared by dehydrating[28] 2-phenyl-2-hydroxybutane in a heated flask packed with glass wool and containing a crystal of iodine. A mixture of olefins and water was distilled off between 160 and 180° (1 atm). Terminal olefins were removed by chromatographing the mixture on a 1 in. diameter column of 200 g of alumina impregnated with 30 g of $AgNO_3$. Subsequent preparative glpc on an SE-30 column at 160° gave pure samples of the *cis* and *trans* olefins with retention times of 54 and 36 min, respectively (lit.[29] bp 193° (*cis*), 174° (*trans*)).

3-Methyl-2-phenyl-2-butene (α,β,β-trimethylstyrene) was prepared as described above by dehydration of the crude alcohol, bp 120–125° (20 mm) (lit.[30] bp 118° (24 mm)), obtained by treating isopropylmagnesium chloride with acetophenone. The olefin layer was distilled (spinning band) and a fraction, bp 178–180° (205 mm) obtained. The nmr spectrum indicated about 17% of a terminal olefin (doublet at 5.05 ppm). This was removed by chromatography on Al_2O_3 impregnated with 10% $AgNO_3$. Further purification was carried out by preparative glpc on the SE-30 column at 130°.

Pure samples of *cis*-2-butene (99.9%) and *trans*-2-butene (99.8%) were obtained from the Philips Petroleum Co., Bartlesville, Okla.

Addition and Isolation Procedures. Procedure i. Initial attempts to examine the products of bromine addition to styrene, 3-chlorostyrene, 3-nitrostyrene, and α-methylstyrene involved addition of microdrops of neat bromine to 50 ml of a stirred olefin solution in acetic acid (8.0×10^{-2} *M*) at 25°. The products were isolated by pouring the reaction mixture into cold saturated NaCl solution (175 ml), followed by extraction with 60–70° petroleum ether or diethyl ether and washing with $NaHCO_3$ solution, then water. The extracts were dried over $MgSO_4$ and concentrated to constant weight on a rotary evaporator at room temperature.

Procedure ii. Because the product distribution obtained was found to depend somewhat on addition procedure, the following method of addition was subsequently generally employed to approach more closely the conditions under which the kinetics were to be investigated. A closed, 3-necked, 25-ml reaction flask equipped with condenser and drying tube was filled with 15 ml of acetic acid and thermostated at 25°. A solution of olefin (5×10^{-3} mol) in 5 ml of solvent was then allowed to drain in through a capillary tube below the surface, with stirring. Simultaneously, through a second capillary, an equivalent amount of neat bromine was added so as to maintain a straw yellow color in the reaction flask. In this way the analytical bromine concentration was kept below 10^{-3} *M* as estimated from the intensity of the yellow solution. The same method of product isolation as in i was used.

Procedure iii. In order to study the effect of high local concentrations of both Br_2 and HBr on the reaction products a third method of addition was sometimes used. An apparatus similar to that in ii was used except that 15 ml of approximately 0.3 *M* Br_2 in acetic acid was first added. The theoretical amount of olefin in 5 ml of acetic acid was then drained in slowly, with stirring. The previously described method of isolation was then used.

Except where noted all results reported were obtained by procedure ii. The reliability of the concentration procedures were tested on solutions of known composition in acetic acid. Subsequent analysis indicated no significant change in composition.

Analytical Procedures. The products concentrated from the reaction mixtures were examined by both infrared and nmr spectroscopy. Percentage compositions were determined from integrated areas of appropriate peaks or from peak height ratios. Both methods gave reliable results (±1%) for most mixtures. Further details of the nmr spectra are given in another section. Separation of products was carried out by glpc using 10 ft × $\frac{1}{4}$ or $\frac{3}{8}$ in. aluminium columns packed with 40–60 mesh commercial Tide detergent except where noted. Tide columns were preconditioned at 170° for 2 days to remove aromatic perfumes. Decomposition of dibromides on the column was minimized by using glass inserts in the injection port and by previously saturating the reaction solvent with oxygen. The latter was shown to have no effect on the product distribution but was subsequently effective in minimizing product isomerization and decomposition on the columns. With these precautions reproducible glpc analyses were obtained in good agreement with those obtained by nmr analysis. The response of the hydrogen flame detector to various different products was checked using standard mixtures. It was found that mole percentage compositions obtained from glpc peak area ratios were reproducible to within 1%.

Identification of Reaction Products from Individual Olefins. Styrene. The crude product from bromination in acetic acid indicated it to be predominantly styrene dibromide from its well characterized nmr spectrum but the infrared spectrum showed the presence of a carbonyl absorption (5.73 μ in CCl_4) which could not be removed by extensive washing with $NaHCO_3$ solution. Chromatography on the Tide column at 140° gave two peaks with retention times 79 and 99 min. These were identified as styrene dibromide and 2-bromo-1-phenylethyl acetate, respectively, by comparison with authentic samples.

Preparation of 2-Bromo-1-phenylethyl Acetate. α-Bromoacetophenone was reduced with 1 equiv of $LiAlH_4$. The crude mixture was acetylated directly by refluxing with excess acetyl chloride. The acetylation mixture was poured onto ice, extracted (60–70° petroleum ether), washed, dried, and concentrated. Distillation of the resulting yellow oil gave a clear liquid, bp 88–90° (0.5 mm) (lit.[31] bp 105–107° (3 mm)). Both its nmr spectrum and retention time were identical with those of the second product from bromination of styrene in acetic acid.

3-Chloro- and 3-Nitrostyrenes. Bromination in each case gave only two products (by glpc analysis). The close similarity of the nmr spectra of these mixtures to that from styrene itself showed these to be clearly the dibromo and 1-acetoxy-2-bromo adducts.

α-Methylstyrene. Addition of bromine yielded three products. In addition to the expected dibromide the infrared spectrum of the mixture showed the presence of both carbonyl and hydroxyl groups. This suggested some hydrolysis was occurring during work-up. A pure sample of the dibromide was stirred in aqueous acetone (10:4, v/v) for 24 hr at room temperature. The crude product was extracted (petroleum ether) and purified by chromatography on a $\frac{1}{2} \times 10$ in. Florisil column. Fractions combined on the basis of their nmr spectra were concentrated and molecular distillation (0.5 mm) gave a pure sample of the bromohydrin, 1-bromo-2-hydroxy-2-phenylpropane. *Anal.* Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15; Br, 37.15. Found: C, 50.45; H, 5.07; Br, 36.99. The infrared spectrum confirmed the presence of a hydroxyl group and the nmr (CCl_4) gave singlets at 1.52 (3.0), 2.92 (1.0), and 3.52 (2.0) with a multiplet at 7.1–7.4 (5.3). Reduction of the bromohydrin with $LiAlH_4$ gave dimethylphenylcarbinol with an nmr spectrum showing a singlet at 1.42 (6.0), singlet at 3.13 (1.0), and phenyl absorption at 7.1–7.5. Acetylation of the bromohydrin with excess acetyl chloride gave on molecular distillation an oil which crystallized on standing, mp 49–50°. *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.62; H, 5.17; Br, 30.64. The nmr spectrum gave singlets at 1.86 (2.9), 2.00 (3.1), 3.80 (1.0), 3.82 (0.9), and a single peak at 7.22 (5.4). The nmr spectra of this bromo acetate (1-bromo-2-acetoxy-2-phenylpropane) and the above bromohydrin were superimposable on those of the two unknown products of bromination of α-methylstyrene.

***cis*- and *trans*-1-Phenylpropenes.** The bromination mixture from each olefin showed the presence of the same products. Three

---

[27] J. Levy and A. Tabart, *Bull. Soc. Chim. France*, **49**, 1776 (1931).

[28] A. S. Brown and M. G. Voronkov, *J. Gen. Chem. USSR*, **17**, 1162 (1947).

[29] A. Klages, *Ber.*, **35**, 2641 (1902); A. Haller and G. Bauer, *Ann. Chim.*, **9**, 12 (1918).

[30] E. E. Blaise and A. Courtot, *Bull. Soc. Chim. France*, **35**, 587 (1906).

[31] C. S. Marvel and N. S. Moon, *J. Am. Chem. Soc.*, **62**, 45 (1940).

peaks were obtained by glpc using the Tide column at 140° with retention times 93, 101, and 107 min. The compound with shortest retention time was shown to be the *erythro*-1,2-dibromo-1-phenylpropane by comparison with an authentic sample. The latter was prepared by recrystallizing the major product of bromine addition to *trans*-β-methylstyrene in CCl_4, mp 66.5–67° (lit.[17] mp 67°). The major product of bromination of *cis*-β-methylstyrene appeared to contain about 85% *threo* dibromide and could not be purified by crystallization. The nmr spectrum of this crude *threo* dibromide was clearly quite different (β-methyl protons) from that of the *erythro* diastereomer and its retention time (107 min) was found to be identical with that of the third reaction product. The remaining product was shown to be either one of the diastereomeric 1-acetoxy-2-bromo adducts or possibly a mixture of both by comparison of the nmr spectrum and glpc retention time with authentic samples.

"*erythro*"-1-Acetoxy-2-bromo-1-phenylpropane was prepared by addition of acetyl hypobromite to *trans*-1-phenylpropene. Silver acetate (1.5 g) recrystallized from water and dried over P_2O_5 at 0.1 mm was stirred with 25 ml of CCl_4 at −20° and 1.4 g of bromine in CCl_4 added slowly. The mixture was allowed to warm to room temperature slowly, then cooled again to −20°. A solution of *trans*-1-phenylpropene (0.95 g) in 15 ml of CCl_4 was added and the reaction mixture warmed to room temperature. After filtering off the AgBr, the filtrate was washed with $NaHCO_3$, then water, dried ($MgSO_4$), and concentrated. Chromatography using petroleum ether–ether mixtures on a $\frac{1}{2} \times 10$ in. Florisil column, followed by concentration of appropriate fractions, then molecular distillation (0.3 mm) gave a clear liquid. The nmr spectrum showed a doublet at 1.55 (2.2), singlet at 1.99 (2.9), multiplet at 4.3 (1.0), doublet at 5.92 (1.0), and singlet at 7.30 (5.2). *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.88; H, 5.31; Br, 31.00. The infrared and nmr spectra of this compound were indistinguishable from those of the 1-acetoxy-2-bromo-1-phenylpropane prepared by acylation of the "*erythro*"-1-hydroxy-2-bromo-1-phenylpropane made by the method of Fischer.[21] The latter compound on treatment with an aqueous acetone–sodium carbonate mixture gave an epoxide with an nmr spectrum showing a doublet (J = 5.0 cps), at 1.35 (3.3), quartet at 2.80 (1.0), a doublet (J = 1.8 cps) at 3.38 (1.0), and phenyl absorption at 7.18. "*threo*"-1-Acetoxy-2-bromo-1-phenylpropane was prepared by addition of acetyl hypobromite to *cis*-1-phenylpropene by the method described above. The nmr spectrum showed a doublet 5.85 (1.0) and a single peak at 7.3. *Anal.* Calcd for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.43; H, 5.23; Br, 31.40. Attempts to separate mixtures of these "*erythro*" and "*threo*" acetoxy bromides on the 10-ft Tide column were unsuccessful, the retention time of the mixture being identical with that of the second bromination product from both *cis*- and *trans*-1-phenylpropenes.

2-Methyl-1-phenylpropene (β,β-Dimethylstyrene). The crude reaction mixture after work-up, was chromatographed on a Florisil column. Elution with 60–70° petroleum ether gave the dibromide which was identified by comparison with a sample prepared by adding bromine to the olefin in dichloromethane. Molecular distillation (0.2 mm) of this product gave a clear liquid. *Anal.* Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14; Br, 54.73. Found: C, 40.58; H, 3.91; Br, 55.75. In addition to the dibromide two additional compounds were removed by elution with benzene–petroleum ether mixtures. These were tentatively assigned as bromo acetates. The first of these A gave a liquid on molecular distillation which crystallized to give a white solid, mp 50–53°. The nmr spectrum gave singlets at 1.68 (5.9), 2.05 (3.2), and 5.85 (1.0) with a multiplet at 7.25–7.45 (5.4). The infrared spectrum showed carbonyl absorption at 5.75 μ. *Anal.* Calcd for $C_{12}H_{15}BrO_2$: C, 53.15; H, 5.58; Br, 29.47. Found: C, 53.56; H, 5.85; Br, 28.81. The second product, C, was an oil, which showed both a hydroxyl and a carbonyl absorption in the infrared. The nmr gave singlets at 1.11 (6.0), 2.05 (3.1), 2.22 (1.0), and 5.57 (1.0), with a phenyl absorption at 7.3. The nmr spectrum in DMSO-d_6 gave the hydroxyl absorption at 4.4 ppm as a broad peak. The α-proton signal was unchanged from that in CCl_4 and remained sharp at 5.6 ppm. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; P, 23.05. Found: C, 69.14; H, 7.94. The acetoxy bromide A and the hydroxy acetate C were identified as follows. 1-Bromo-2-hydroxy-2-methyl-1-phenylpropane was prepared by refluxing benzyldimethylcarbinol (1.0 g) in CCl_4 for 2 hr with 1 equiv of N-bromosuccinimide. After work-up a crude oil was isolated and chromatographed on the Florisil column (50:50, v/v benzene–petroleum ether). Molecular distillation (0.5 mm) gave a white solid, mp 68–69°, with nmr spectrum showing singlets at 1.24 and 1.30 (6.1), 2.11 (0.9), 4.89 (1.0), and phenyl absorption at 7.1–7.5 (5.3). *Anal.* Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br, 34.88. Found: C, 52.40; H, 5.75; Br, 34.89. Acetylation of this bromohydrin with excess acetyl chloride, followed by molecular distillation of the product gave an oil, whose nmr spectrum showed singlets at 1.51 (6.0), 1.90 (3.1), 5.58 (1.0), and phenyl absorption at 7.1–7.5 (5.5). *Anal.* Calcd for $C_{12}H_{15}BrO_2$: C, 53.16; H, 5.58; Br, 29.47. Found: C, 54.28; H, 5.79; Br, 29.00. Since 1-bromo-2-acetoxy-2-methyl-1-phenylpropane is not identical with the bromination product A, the latter must be 2-bromo-1-acetoxy-2-methyl-1-phenylpropane. Treatment of a sample of 1-bromo-2-acetoxy-2-methyl-1-phenylpropane (B) under the conditions used to separate the crude reaction products have a hydroxy acetate which was indistinguishable from compound C, which is thus 1-hydroxy-2-acetoxy-2-methyl-1-phenylpropane.

3-Methyl-2-phenyl-2-butene (α,β,β-Trimethylstyrene). Bromination gave several products, one of which was identified as the dibromide by comparison with the sole product of bromination in dichloromethane. This was purified by molecular distillation and its nmr spectrum gave singlets at 1.90 (3.2), 2.12 (2.9), and 2.50 (3.0), with broad and complex phenyl absorption at 7.2–7.8. The presence of acetoxy bromides in the crude reaction product from acetic acid was shown from the infrared absorption at 5.75 μ, but no attempt was made to separate or identify these compounds.

***cis*- and *trans*-2-Phenyl-2-butenes.** The crude reaction product from each olefin was largely a mixture of two dibromides. The major component from the *cis* olefin was characterized by two methyl absorptions, a singlet at 2.19 and a doublet at 1.96 (J = 6.5 cps). This was identical with the minor component from the *trans* olefin. The major dibromide from the *trans* olefin also showed two methyl absorptions, a singlet at 2.29 and a doublet at 1.56 (J = 7.0 cps). This was identical with the minor component from the *cis* olefin. The nmr spectra of these diastereomers is discussed in the Results. The infrared spectra of the crude products showed carbonyl absorption indicating that acetoxy bromides had also been formed. No attempt was made to characterize these minor products.

***cis*- and *trans*-2-Butenes.** Samples of the pure diastereomeric dibromides were prepared by adding bromine to each olefin in dichloromethane at −60°. The dibromides prepared in this manner contained less than 1% of the other diastereomer as determined by glpc (Tide column at 85°), the *cis* olefin giving only *dl*-2,3-dibromobutane and the *trans* olefin only *meso*-2,3-dibromobutane.[9] The reaction products in acetic acid showed that only one dibromide was formed from each olefin. Small amounts of acetoxy bromides were formed in each case, as shown by the presence of carbonyl absorption in the infrared spectra of the crude reaction mixture, but in insufficient quantities to allow definite characterization.

Olefin and Dibromide Stabilities. Possible isomerization of *cis*- and *trans*-1-phenylpropenes under the reaction conditions was checked by allowing the olefins to stand in acetic acid for several hours at 25°. Recovery of the olefins and subsequent glpc analysis showed no isomerization had occurred. However in acetic acid with 5% HBr added, the *cis* olefin was found to 85% isomerized in 45 min at 25°. The possibility of such isomerization under bromination conditions was checked by squirting a twofold excess of neat olefin into a vigorously stirred 25 ml solution of bromine (0.1 M) in acetic acid at 25°. The reaction was rapid and exothermic (10° rise). Analysis of the reaction products by glpc showed that only 1–2% of unreacted olefin had isomerized to the *trans* olefin. Similar experiments on the *trans* olefin showed no isomerization of the unreacted olefin. The stability of the dibromides from styrene, β,β-dimethylstyrene, and *cis*- and *trans*-1-phenylpropenes was investigated by allowing them to stand in both acetic acid and acetic acid containing 0.1 M $LiClO_4$ for at least 1 hr. No evidence of acetolysis products was found from the nmr spectra or glpc analysis. A sample of styrene dibromide was heated for 10 hr at 90° in acetic acid then allowed to stand for a further 30 hr at room temperature. Analysis indicated less than 4% of 2-bromo-1-phenyl acetate had been formed.

Acknowledgments. The continued financial support of the National Research Council of Canada and the award of Studentships to J. H. R. are gratefully acknowledged.