(24) Initially, we reported[1] that **6** was a precursor of **7**.
(25) R. C. Paul, R. Kaushal, and S. S. Pahil, *J. Indian Chem. Soc.*, **44**, 995–1000 (1967), and work cited therein.
(26) D. Bauer and A. Foucault, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 192–194 (1971).
(27) S. Swan, Jr., in "Techniques of Organic Chemistry", Vol. II, A. Weissberger, Ed., Interscience, New York, N.Y., 1956, p 393.
(28) D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, *J. Org. Chem.*, **23**, 1412–1419 (1958).
(29) R. H. Carter (nee' Rayner), R. M. Colyer, R. A. Hill, and J. Staunton, *J. Chem. Soc., Perkin Trans. 1*, 1438–1441 (1976), and references cited therein. A new approach to these structures via π-olefin–metal complexes has recently been reported: D. E. Korte, L. S. Hegedus, and R. K. Wirth, *J. Org. Chem.*, **42**, 1329–1336 (1977).
(30) Melting points are uncorrected. Elemental analyses were performed under the direction of Mr. J. P. Gilbert of these laboratories. The "usual workup" involves aqueous washing of the organic solvent solutions followed by drying over sodium or magnesium sulfate then evaporation to dryness in vacuo.
(31) We thank Mr. W. E. Shearin for this preparation.

Substituent Effects on Bromodecarboxylation Reactions

Charles A. Kingsbury* and George Max

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

Received September 17, 1976

The reaction of ring-substituted cinnamate and α-methylcinnamate ions with bromine in water or methanol was studied. Where strongly electron-donating substituents were present, the decarboxylation products, 1-bromo-2-phenylethene or 2-bromo-1-phenyl-1-propene, were predominant. With groups of indifferent electronic character, considerable β-lactone was observed. With electron-withdrawing groups (cinnamate ions) the predominant products result from solvent capture of the intermediate ion. The effects of temperature and bromide ion concentration are discussed. The stereochemistry of the conversion to lactone and olefin is interpreted in terms of the least motion of the intermediate ion to arrive at a conformation capable of forming products. An improved synthesis of cinnamic acids is given.

The problem of interest concerns the reactions of bromine with various substituted cinnamate ions (Scheme I). The reaction very likely proceeds through the intermediate cation (e.g., **2**, Scheme I) although contributions from an electron transfer, or a free-radical pathway, cannot be entirely ruled out.[1] Subsequent reactions of the intermediate carbonium ion **2** include two variations not possible in simple solvolyses,[2] namely decarboxylation and lactonization. Previous work on cinnamic acids includes the rates of halogenation studied by James and co-workers.[3] Tarbell and Bartlett apparently were the first to observe β-lactone formation from the treatment of α,β-unsaturated acids with bromine.[4] Berman and Price studied the reactions of the isomeric α-phenylcinnamate anions with bromine and concluded that the decarboxylation was stereospecific (retention).[5] Lactonization was considered but the importance of this intermediate or product was not clarified. More recently, Johnson and co-workers studied the chlorination of various α,β-unsaturated carbonyl compounds.[6] These workers postulated a concerted chlorodecarboxylation of *trans*-cinnamate ions or, alternatively, decarboxylation passing through a very short-lived intermediate analogous to **2**, since the olefin product was formed with high stereoselectivity, whereas the other reaction products were stereochemically mixed. Lactone was not reported. On the other hand, Berman and Price observed mixed isomeric olefins from treatment of *cis*-cinnamate with bromine.

In view of other work, the absence of β-lactone seems surprising.[4,7,8] The purpose of this work was to study the effects upon the yields and stereochemistry of decarboxylation product, lactone (if any), and solvent capture products as the following parameters are varied: (1) aromatic substituent X and vinyl substituent R; (2) bromide ion concentration; (3) temperature; and (4) solvent.

α-Methylcinnamate Ions (1a); Products of Reaction. Substrate **1a** (R = CH_3) reacts with bromine in the solvents water or methanol to form products **4, 5, 6, 10, 11**, and in certain cases **12** and **13** shown in Scheme I. Tables I and II list the yields of the major products.

For substrates with strongly electron donating groups X, the predominant reaction was decarboxylation to form the olefin **4**. The yield of **4** diminishes as X becomes progressively more electron withdrawing (90% **4** for X = *p*-CH_3O to 2% for X = *p*-Cl in water as solvent). In methanol, the trend is similar.

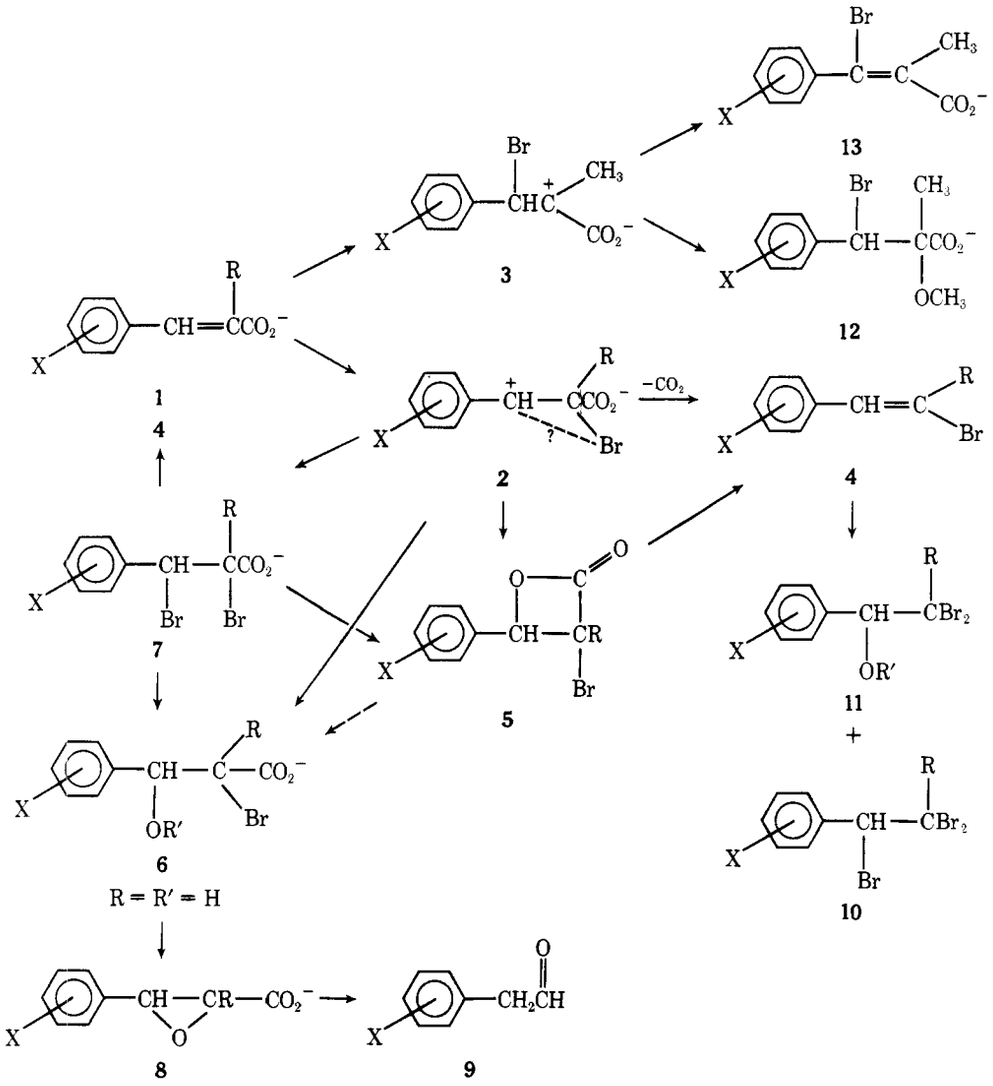
For the same substituent change, the bromohydrin or bromo ether **6** is formed in progressively higher yields (8% for X = *p*-CH_3O to 40% for X = *p*-Cl in water). Lactone **5** is definitely formed in many of these reactions. The yield of **5** is maximum for X = *p*-CH_3 in both solvents. The yields of **5** were rather variable in water, perhaps due to the lability of this product. No more than a trace of **5** is found where X = *p*-CH_3O, perhaps due to the facile reionization and subsequent decarboxylation (**5** → **2** → **4**).[9]

For compounds with electron-withdrawing groups, several additional products are observed by NMR (Figure 1), usually in very small yield. In two cases, the structure has been identified. For X = *p*-NO_2, an acidic product is formed in ca. 46% yield, whose NMR spectrum shows only methyl (δ 2.22) and aromatic absorptions. The olefinic structure **13** is assigned to this product which is also the product of solvolysis of **7** (free acid). For X = *p*-Cl and H, a second acidic product is formed, which shows methyl (δ 1.37), methoxyl (δ 3.49), and methine (δ 5.42) absorptions. The yield of this product is diminished by added bromide. The inverse addition structure **12** is assigned to this product, whose yield would be reduced by reaction of its precursor **3** with bromide. The appearance of **12** and **13** suggests that formation of ion **3** becomes competitive with formation of the benzylic ion **2**, as X becomes electron withdrawing. Solvolysis studies by Hughes and Ingold showed that ions of similar constitution as **3** (i.e., "α-lactones") enjoyed considerable stability, perhaps due to charge attraction in the zwitterion.[10,11] Reaction of the free acid of **1a** (various substituents) with bromine leads to **7** and the normal addition product **6** (no **13**), which suggests that **3** is stable as a zwitterion, but not as a simple cation.

In methanol, a sizable amount of a third material of unknown structure (labeled **6′** in Figure 1) is observed. The methyl chemical shift is very close to the bromohydrin **6** or to

0022-3263/78/1943-3131$01.00/0

Scheme I



threo-bromo ether **6** in both ^{13}C and ^{1}H spectra. This material may be the *threo*-bromohydrin that results from acyl–oxygen cleavage of the lactone, perhaps during workup.

Stereochemistry. The stereochemistry of reaction of substrate **1a** (X = CH_3O) was nonspecific. Approximately equal yields of the cis and trans olefins **4** were observed in either solvent. Mixed isomers of the bromo ethers **6** (60% erythro and 40% threo) were also found. For X = CH_3, observation of the stereochemistry of the olefin was impeded by the overlapping of NMR and GLC peaks. The lactone **5** and the bromo ether **6** were predominantly (>90%) the trans and erythro isomers, respectively. For X = H and Cl, the trans isomers of **4** and **5** and the erythro isomer of **6** were also strongly predominant. The lactone **5** formed from bromine addition to *trans*-**1a** was the same isomer as that formed in the solvolysis of *threo*-**7**. Since **7** forms lactone by intramolecular displacement of bromide, the trans configuration of **5** is indicated. The various stereochemical relationships are depicted in Scheme II.

Effect of Bromide. For X = H and Cl, addition of sodium bromide leads to the formation of ca. 20% dibromide **7** at the expense of **6** (Table I). With 0.6 M sodium bromide, both the cis and trans isomers of the olefin **4** were observed in similar yields in addition to **10** and **11** which could have been derived from either isomer.[12] Since *erythro*-**7** is also present in the reaction mixture and since **7** reacts to form *cis*-**4**, the origin of the cis isomer might be thus explained.

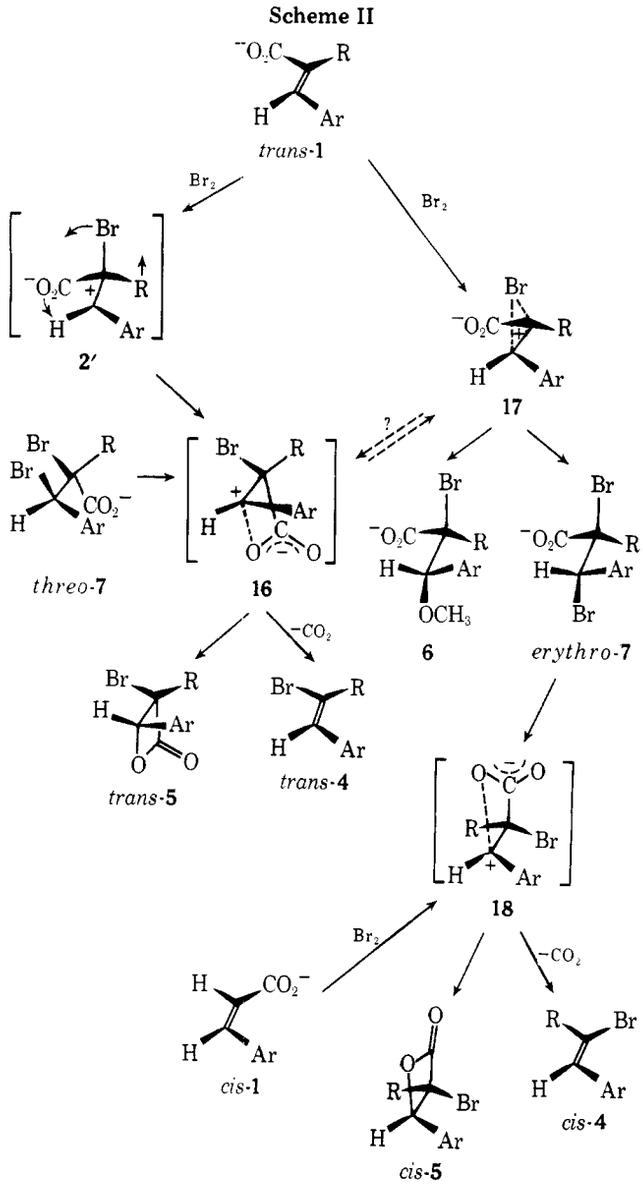
The increase in yield of the olefin **4** in the presence of bromide where X = *p*-CH_3O might thus be explained by the sequence **1** → **7** → **4**. However, the half-lives for solvolysis of **7a** (X = *p*-CH_3O, *m*-Br, H, and Cl) are 7, 88, and 104 min, respectively (at 32 °C), which are far greater than the reaction time, <3 min. On the other hand, a control experiment showed that **7a** (X = *p*-CH_3O, *m*-Br) was definitely reactive in less than 1 min in methanol solutions in the presence of bromine. It is noteworthy that Brown and Russell reported that bromine acts as a Lewis acid catalyst in certain situations, and this property may accelerate the reaction of **7a**.[13]

It is rather difficult to assess the effect of bromide on the yields of the olefin **4** and the lactone **5**, as the changes are about the same as experimental error. At best, a small reduction of yield is observed, especially in the case of electron withdrawing groups X.

Effect of Temperature. The effect of temperature on product yields is recorded in Table IV. At higher temperature, the yield of olefin **4** is increased. The temperature effect on the yields of **5** and **6** is irregular, but the sum of the two changes inversely as the olefin yield. At lower temperature, **4a** (X = H) appears to approach a minimum value, ~9%.

Cinnamate Ions (1b): Products of Reaction. The reactions of **1b** (R = H) are much less satisfactory on a quantitative basis than reactions of **1a**. Acceptable mass balances were difficult to achieve in methanol and impossible in water. The yields appear to be sensitive to seemingly minor variations in

Scheme II



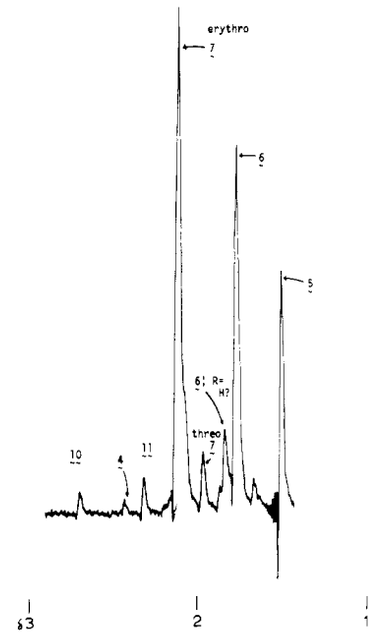


Figure 1. Partial 100 MHz NMR spectrum of the reaction products from treatment of **1a** (X = H) with bromine in methanol as solvent in the presence of NaBr.

procedure. The yields quoted below are applicable for the specific procedure given in the Experimental Section. These data are included because of the availability of the cis isomer (X = *o*-Cl). The point we wish to emphasize in reporting these data is that the stereochemistry of reaction is similar to that of **1a**, despite the presence of a less sterically demanding group, R = H. The trends in the product yields are also rather similar to those from **1a** in most respects.

In methanol, the yield of **4** again diminishes as X becomes increasingly electron withdrawing (73% for X = *p*-CH_3O to 0% for X = *m*-NO_2). Similar trends occur for reactions in water, although the yields are about 20% lower for substrates that from **4**. For the same substituent change, the bromo ether **6** is found in progressively higher yields (21% for *p*-CH_3O to 63% for *m*-NO_2). In water, the bromohydrin **6** is inefficiently removed from the aqueous layer in the workup procedure and yields cannot be quoted.

The lactone **5** is once again definitely formed, although the yields are much smaller than in the case of **1a**. In water, the maximum yield occurred for X = H (18%), whereas in methanol, very little lactone was found for this substrate. In methanol, the maximum yield of **5** was found for X = *o*-Cl (12%). In our hands, the highest yields of **5b** are observed for reactions in ethanol as solvent (26% for X = H and 20% for X = *o*-Cl). The lower ionizing power of ethanol may inhibit opening of the lactone to reform the zwitterion **2**. The relatively high yields in water, which has high ionizing power, may be due to the presence of carbon tetrachloride as a separate phase. The lactone dissolves in CCl_4 upon formation, which may protect it in part from destruction. The reaction time is also very short in water (<1 min). Yields are lower where carbon tetrachloride is omitted. A control experiment showed that a suspension of **5** and **4** (19 and 21% respectively of the amount of **1b** (X = H)) formed 2% **5** and 35% **4** on stirring in water at room temperature for ca. 25 min. Because of the lability of **5**, temperature effects were not extensively investigated (cf. Table IV).

In more highly basic solutions in water (pH ~9 rather than pH ~7), substantial yields of the epoxide **8** were observed (e.g., 40% **8**, where X = *o*-Cl).[14] Phenylacetaldehyde was also observed in certain cases (e.g., 10–13% for X = H). This product is probably formed from the epoxide **8** by a Darzens reaction during workup. This product was rarely observed in reactions run at the lower pH in which epoxides were absent.

Stereochemistry. The steric course of the reactions of **1b** was selective in nature. For *trans*-**1b** (all substituents), only the trans isomer of **4** was observed. In one large-scale run (X = H), the NMR spectrum of a neat sample of the neutral products of reactions showed no observable *cis*-**4**. However, for X = *p*-CH_3O and CH_3, considerable tribromide **10** was observed. Since the more reactive *cis*-**4** would have preferentially formed **10**, no decision about stereochemistry is possible for these substrates. The lactone **5**, where observed, was the trans isomer. The bromo ether **6** was the erythro isomer to the limits of detection, except in the case of X = CH_3O, where similar amounts of *erythro*- and *threo*-**6** were observed. This represents one of the major differences between this study and the chlorine additions reported by Cabaliero and Johnson where mixed products analogous to **6** were found for various substituents X.[6]

For *cis*-**1b** (X = *o*-Cl), reaction with bromine yielded observable amounts of only the cis isomer of the olefin **4** in low yield in both solvents. The cis lactone **5** was also observed in about 6% yield along with traces of *trans*-**5**. The *threo*-bromo ether **6** was dominant (*erythro*-**6**, <5%). There was slight isomerization of the starting material during the course of the reaction.[15]

Table I. Product Yields (%) from Reaction of α-Methylcinnamate Ions 1a with Bromine in Water at 28 ± 3 °C, pH 7.0–8.0

X (salt)[d]	no. of runs	olefin 4[a]	lactone 5	bromohydrin 6	other
p-CH_3O	3	90 ± 1[e]	trace	8 ± 2	
p-CH_3O (Br^-)[d]	1	90		9	
p-CH_3	2	19 ± 1	57 ± 2	22 ± 4	
p-CH_3 (Br^-)	1	16	58	12	3% 7
H	5	6 ± 3	42 ± 10	31 ± 9	
H (Br^-)	2	7 ± 1[b]	46 ± 11	14 ± 10	14 ± 2% 7
p-Cl	2	2 ± 1	41 ± 1	40 ± 2	
p-Cl (Br^-)	2	7 ± 2[c]	38 ± 7	7 ± 3	19% 7, 5% 12
o-Cl	4	8 ± 3	25 ± 7	39 ± 12	8 ± 3% 12

[a] Includes 10 and 11 which are derived from 4. [b] Ca. 50% *cis*- and 50% *trans*-4 were observed. [c] Ca. 60% *cis*- and 40% *trans*-4 were observed. [d] 0.6 M sodium bromide present. [e] In this table, and in Tables II–IV, the error term indicates the maximum range of yields between individual runs.

Table II. Product Yields (%) from Reaction of α-Methylcinnamate Ions (1a) with Bromine in Methanol at 28 ± 3 °C

X (salt)[e]	no. of runs	olefin[a] 4	lactone 5	bromo ether 6	other
p-CH_3O	4	77 ± 5	trace	22 ± 5	
p-CH_3O (Br^-)[e]	1	90		10	
p-CH_3	3	16 ± 1	47 ± 3	35 ± 3	
p-CH_3 (Br^-)	1	27	49	11	12% 7
H	4	12 ± 5	23 ± 3	55 ± 8	ca. 6% 12
H (0.6 M Br^-)[f]	1	12[b]	16	31	35% 7, ca. 2% 12
H (1.2 M Br^-)	1	9	18	20	45% 7[g]
p-Cl	3	12 ± 3	17 ± 1	45 ± 4	ca. 12% 12, ca. 3% 13
p-Cl (Br^-)[f]	3	7 ± 1[c]	17 ± 2	25 ± 5	20 ± 1% 7, ca. 1% 13, ca. 4% 12
p-NO_2[d]	2	trace	3 ± 3	8 ± 3	46 ± 10% 13, 18 ± 10% 12

[a] Includes 10 and 11. [b] 67% *cis*- and 33% *trans*-4. [c] 50% *cis*- and 50% *trans*-4. [d] Lack of reactivity led to difficultly reproducible data. [e] 0.6 M sodium bromide present. [f] In some runs, a trace of *threo*-7 appeared to be present. The very small yields (<5%) made positive identification difficult. [g] Ca. 10% threo and 90% erythro isomers.

Table III. Product Yields (%) from Reaction of Cinnamate Ion (1b) and Bromine in Methanol at 28 ± 3 °C

X (salt)[c]	no. of runs	olefin 4[a]	lactone 5	bromo ether 6	dibromide 7
p-CH_3O	3	73 ± 4		21 ± 2	
p-CH_3O (Br^-)[c]	1	89		4	
o-CH_3O	2	58 ± 5		26 ± 8	
o-CH_3O (Br^-)	2	65 ± 5		30 ± 5	
p-CH_3	3	47 ± 1	trace	55 ± 3	
p-CH_3 (Br^-)	1	41		49	2
H	2	23 ± 2	trace	63 ± 2	
H (Br^-)	3	20 ± 4	trace	40 ± 6	19 ± 4
p-Cl	3	14 ± 4	3 ± 1	62 ± 4	
p-Cl (Br^-)	1	19		41	36
trans-*o*-Cl	2	trace	12 ± 3	56 ± 5	4 ± 2
trans-*o*-Cl (Br^-)	3	2 ± 2	9 ± 2	25 ± 3	41 ± 11
cis-*o*-Cl	2	6 ± 2	6 ± 2[b]	70 ± 5	
cis-*o*-Cl (Br^-)	1	9	6	17	43
m-NO_2	2		2 ± 2	63 ± 2	28 ± 8

[a] Includes 10 and 11 which are derived from 4. [b] Total of two isomeric structures. [c] 0.6 M sodium bromide present.

Effect of Bromide. Addition of sodium bromide again reduced the yields of the bromo ethers 6 by 17–30% (Table III) for X = CH_3, H, and *p*-Cl. In the case of X = *p*-CH_3O, the yield of olefin 4 was again increased by added bromide. Control experiments showed that the dibromide 7 was labile under the reaction conditions. Otherwise, the effect of bromide on olefin 4 and lactone 5 yields is at best a slight reduction, although the changes are usually within experimental error.

Discussion. Generally, the results of this study are in agreement with the findings of Berman and Price who observed retention of configuration in bromodecarboxylation,[5] with the added feature that predominant "retention" in lactone formation is also observed (e.g., *trans*-1b forms *trans*-5b). The chief exception to this specificity is where strongly stabilized ions (e.g., 2, X = *p*-CH_3O) undergo internal rotation prior to decarboxylation. The ensuing discussion excludes *p*-CH_3O substituents.

The effect of added bromide ion on the yields of olefin 4 and lactone 5 is small and much less than the effect on the yields of bromo ether 6. These data are in agreement with the findings of Cabaliero and Johnson, who suggested a concerted or very rapid stepwise process for the formation of 4b.[6] Thus, bromide does not appear to be able to intercept the precursor of 4 or 5. However, the high stereospecificity with which 6 is formed shows that the precursor does not attain rotational equilibrium, although the precursor is sufficiently long lived

Table IV. Effect of Temperature on Product Yields (%) in Methanol Solvent

substrate	X	no. of runs	temp,[a]	olefin 4	lactone 5	6	other
1a	p-CH_3O	3	28	77 ± 5	trace	22 ± 5	
	p-CH_3O	1	0	73		27	
	p-CH_3O	1	−77	52		48	
1a	H	2	67	27 ± 2	22 ± 5	33 ± 8	8 ± 3% 13
	H	4	28	12 ± 5	23 ± 3	55 ± 8	6 ± 4% 13
	H	2	−3	9 ± 1	19 ± 3	52 ± 3	5 ± 1% 13
	H	2	−75	9 ± 2	35 ± 5	47 ± 14	7 ± 4% 13
1a	p-Cl	2	67	16 ± 1	28 ± 1	46 ± 7	12 ± 5% 13
	p-Cl	3	28	12 ± 3	17 ± 1	45 ± 4	12 ± 6% 13
	p-Cl	2	−4	11 ± 2	23 ± 2	61 ± 6	13 ± 5% 13
	p-Cl	1	−75	unreactive			
1b	p-CH_3O	3	28	73 ± 4		21 ± 2	
	p-CH_3O	1	2	73		20	
1b	H	2	65	33 ± 1		57 ± 7	
	H	2	28	23 ± 2	trace	63 ± 2	
	H	2	2	22 ± 3	3 ± 2	67 ± 2	

[a] Temperature limit ±3 °C.

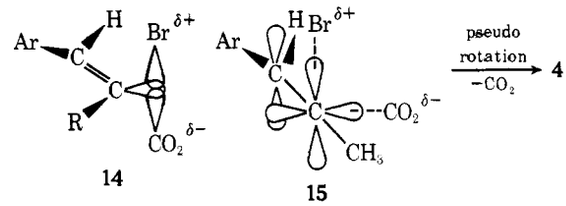
to selectively react with bromide to form **7** rather than react with one of the large number of solvent molecules present. A bridged bromonium ion (**17**) is highly likely, especially in cases where X is electron withdrawing.[16] The poorer neighboring group, chlorine, does not maintain stereochemistry in Johnson's cases.[6]

The question remains concerning the identity of the precursor of the olefin **4**. The main difficulty with a concerted mechanism may be intellectual, and not chemical; namely, it is difficult to envision an adequate concerted mechanism. One possibility is **14**, which displays a three-center two-electron bond.[12a,17] However, this transition state does not account for the effect of X. An alternative intermediate or transition state, **15**, displays effective sp^1 hybridization at the carbon undergoing covalency change.[18] This structure does not account for the stereospecificity, as pseudorotation in either direction may occur. Neither **14** nor **15** readily explain the similar stereochemistry and (lack of) sensitivity to bromide in the formation of **4** and **5**. Thus, rapid stepwise mechanisms must be considered as alternatives to try to identify common intermediates that link the 1 → **4** and 1 → **5** processes (cf. Scheme II).

The precursor of **4** and **5** is considered to be an ion basically similar to **2** (Scheme I). To explain the stereospecificity of formation of **4** and **5**, this ion must be able to preserve stereochemistry, but in a different way than **17**. The ion **16** is believed to be stabilized by electrostatic participation and possibly a degree of covalent bonding between COO^- and the β carbon. Vaughan and co-workers have quite conclusively demonstrated the importance of such electrostatic participation.[10b]

As bromine approaches and bonds to **1** (possibly via a π complex),[16f] charge attraction develops between the COO^- and the position of greatest positive charge density (the β carbon). This attraction leads to a "least-motion" process[19] in which a 60° rotation of the α carbon occurs (Scheme II) placing the COO^- in an optimum orientation for electrostatic participation. No products from the alternative ion **18** were observable, and thus the alternative 120° rotation is apparently disfavored.

The rapid reaction of **16**, despite the fact that this ion must be more stable than **17** for certain substituents, is explicable in terms of the idea that the orientation of COO^- that is optimum for electrostatic participation (**16**) is also optimum for decarboxylation and/or ring closure to form the lactone. These unimolecular processes may be intrinsically more rapid than



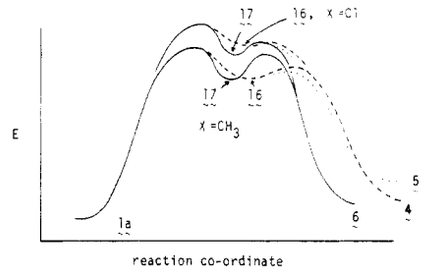
14 **15**

capture of **16** by a molecule of solvent to form *threo*-**6**. The low barrier for the **16** → **4** and **16** → **5** processes[20] and the relative energies of **16** and **17** as X varies are shown in Scheme III.

Reactions of α-Methylcinnamate Dibromides (7a). The reactions of **7a** are of interest since many of the same intermediates are possible as in the bromination of **1a**.[21] In addition, a concerted E2-like debromodecarboxylation may also occur.[22,23] A time study of the reaction of *threo*-**7a** (X = H) is given in Figure 2. A trans lactone intermediate (**5**) is observed, which builds up to a maximum level of 16% of the total integration then decays to zero. The major product is *trans*-**4** (81%), plus some bromo ether **6** (ca. 3%) and an unknown material (ca. 9%). The appearance of the unknown material is suppressed by running the reaction in the presence of LiBr. The chemical shifts of the unknown are rather similar to **12**, discussed earlier. The unknown may be the other diastereomer, presumably *threo*-**12**.

Direct observation of the course of reaction of *erythro*-**7a** (X = p-CH_3, H, or p-Cl) in methanol, or preferably, methanol-d_4, showed the rise and decay of peaks at δ 2.16 (CH_3) and δ 5.64 (CH) which can be ascribed to the cis lactone **5**. The chemical shifts for methyl of *cis*- and *trans*-**5** bear the same relationship to one another as the authentic cis and trans lactones (H replacing Br in **5**) prepared by Noyce and Banitt.[9b] For X = p-CH_3, **5** builds up to a maximum of about 10% of the total. The product mixture is again rich in **4** (~80% *cis*-**4** for

Scheme III



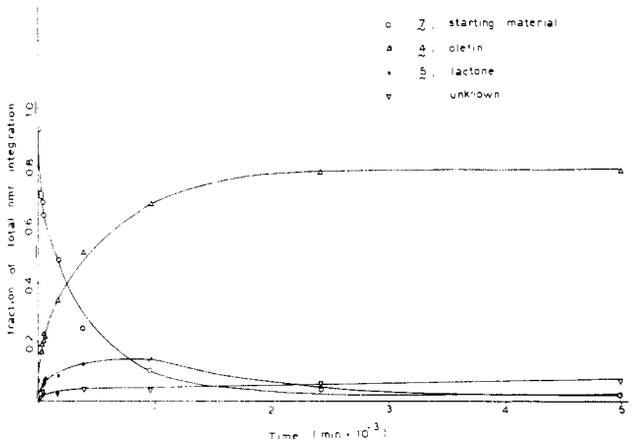


Figure 2. Time study of the solvolysis of *threo*-**7a** (X = H) in methanol-d_4 at room temperature as observed by NMR.

most substrates). Some **1a** appears very early in the reaction sequence and its level does not thereafter change.

The debromodecarboxylation of **7b** was studied earlier by Bordwell and Knipe, who cautiously disfavored the E2 process and preferred the E1 process, which proceeds through a zwitterion similar to **2**.[24] This preference resulted from a rate dependence upon σ^+ parameters and a similarity of **7b** in activation and Hammett ρ parameters to a substrate that could react only by a zwitterionic intermediate. No evidence could be found for two primary processes.[22] Earlier, Trumbull and co-workers found that electron-withdrawing groups in **7b** led to formation of *cis*-**4**, particularly in solvents of low ionizing power, whereas electron-donating groups X led to formation of the more stable *trans*-**4**.[22] These results were interpreted in terms of a dual mechanism originally proposed by Cristol and Norris (i.e., mostly E1 for X = p-CH_3O and mostly E2 for X = p-NO_2).[14] Bordwell and Knipe interpreted these results in terms of an E1 process in which electrostatic participation by carboxylate was tight or loose (permitting internal rotation) depending on X and solvent.

In the case of **7a**, neither Hammett σ nor Brown–Okamoto σ^+ parameters gave linear plots vs. log k (Table VI).[1b] Moving from methanol as solvent to 60% dimethyl sulfoxide (Me_2SO)–40% methanol resulted in a rate increase of 200, 330, and 710 for X = H, p-Cl, and p-NO_2, respectively. Thus the p-Cl compound surpasses X = H in reactivity. The substrate with X = p-NO_2 also approaches X = H in reactivity, but X = p-NO_2 undergoes a mechanism change giving ca. 80% **13** in 60% Me_2SO. The substrate with X = p-Cl also forms some **13** (ca. 13%) but still mostly **4** in 60% Me_2SO. Me_2SO, as solvent, does not readily support carbonium ion reactions, although many types of anionic (e.g., E2) reactions occur at markedly increased rates in Me_2SO mixtures.[26] The really definitive test of mechanism, however, would appear to be the presence or absence of a ^{13}C isotope effect for debromodecarboxylation.[27] We will defer judgment concerning mechanism until this experiment is performed.

The main question concerns the different stereochemistry in the reactions of **7a** in contrast to the bromine additions to **1a** and the higher level of olefin **4a** in the former reaction. To recapitulate, addition of bromine to *trans*-**1a** forms *trans*-**4**, *trans*-**5**, and *erythro*-**6** (or **7**). Reaction of the *erythro*-dibromide **7a** yields *cis*-**4** and *cis*-**5**. Presuming Bordwell's ideas concerning electrostatic participation to be correct, the stereochemistry of reaction of **7a** to form *cis*-**4** and **5** seems best explained in terms of the intermediate ion **18** (Scheme II). The approach of carboxylate from the other side of the molecule (to form **16**) is blocked by the leaving group. Therein lies the major difference between **7a** and the least-motion process in bromine addition to **1a** in which **16** is directly formed.

Table V

substrate	X	yield, %	mp, °C	lit. mp, °C (ref)
1a	p-CH_3O	26	158–159	157 (30)
	p-CH_3	41	169–171	169–170 (31)
	H	86	79–80	78 (31)
	p-Cl	45	168–172	168–169 (32)
	p-NO_2	33	208–210	208 (33)
1b	p-CH_3O	96	172–174	173 (35)
	o-CH_3O	86	181–183	185 (35)
	p-CH_3	92	197–198	198 (36)
	H	90	131–132	133 (34)
	o-Cl	93	201–204	211 (37)
	m-NO_2	80	201–203	203 (38)
	p-NO_2	88	287–289	286 (38)

Experimental Section

α-Methylcinnamic Acids (1a). The various substrates **1a** were prepared by the Perkin reaction.[29] A list of the substrates prepared and other data are given in Table V, including **1b** discussed below.

Cinnamic Acids (1b). An improvement on the Doebner modification of the Knoevenagel reaction is indicated below, making cinnamic acids one of the simplest preparations known.[29] To a mixture of 10.0 g (0.072 mol) of p-chlorobenzaldehyde and 0.83 g (0.08 mol) of malonic acid dissolved in 25 mL of dimethyl sulfoxide, 1 mL of piperidine was added. After an initial exothermic reaction subsided, the mixture was heated on a steam bath (ca. 80 °C) overnight (ca. 10 h). The mixture was poured onto 200 g of ice, and the resulting slurry was acidified with 6 N HCl. After the ice melted, the mixture was filtered and the solid cinnamic acid was washed repeatedly with water. If an odor was apparent, the solid product was also washed with petroleum ether. The product was air dried, yielding 11.4 g (87%) of **1a** (X = p-Cl), mp 246–248 °C (lit.[34] mp 250 °C). No impurities were evident in the NMR spectrum. The product was usually pure enough to be used directly, although in some preparations a single recrystallization was necessary.

Various commercial brands of dimethyl sulfoxide were used as received; these resulted in similar yields of product. It is important not to let the temperature of the reaction go too high, as evil smelling decomposition products of Me_2SO will adhere to the product. The yield may be improved slightly by using an excess of malonic acid, but the advantage does not outweigh the cost. Piperidine appeared to be the best of the bases tried. In no case was any trace of benzalmalonic acid found.

***cis-o*-Chlorocinnamic acid** was prepared by photolyzing the trans isomer in a quartz flask with a 100 W Hanovia lamp for ca. 1 week. The solvent was dichloromethane and the solution was under nitrogen. The solvent was partially evaporated, and the mixture was crystallized in a sacrificial manner, rejecting the trans isomer that preferentially crystallized. The resulting product showed traces of the trans isomer, mp 136–137 °C (lit.[38] mp 138–139 °C).

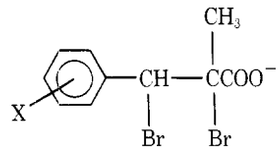
α-Methylcinnamic Acid Dibromides (7a). These were prepared by the Sudborough procedure[39] (A) or by the Trumbull procedure[24a] (B). The p-methoxy-m-bromocinnamic acid dibromide was prepared by procedure A, by placing the p-methoxy acid (11.5 g., 0.06 mol) in a desiccator, along with a beaker of H_2SO_4 and a beaker of bromine. The solid p-methoxy acid was removed at intervals and weighed. When it had reacted with the theoretical quantity of bromine vapor, it was removed and recrystallized from chloroform–pentane, mp 196–197 °C, 17 g (67% yield). This acid was found to have brominated in the aromatic ring, as shown by the ABX aromatic proton NMR pattern and the analysis.

Anal. Calcd for $C_{11}H_{11}Br_3O_3$: C, 30.66; H, 2.57. Found, C, 31.00; H, 2.89.

Unsubstituted α-methylcinnamic acid dibromide was prepared by procedure B by treating 12.7 g of α-methylcinnamic acid (0.08 mol) in 250 mL of glacial acetic acid with bromine (12.5 g, 0.08 mol). The mixture was heated to gentle reflux and stirred for 4 h. About half of the solvent was removed by rotary evaporation and the remainder was poured into water. The precipitate was quickly filtered and recrystallized from chloroform–pentane, after drying ($MgSO_4$), mp 141–143 °C (lit.[40] mp 137 °C), yielding 12.2 g (48%).

The p-methyl acid was prepared by procedure A in 96% yield, mp 160–161 °C.

Table VI. Rates of Reactions of the Anions of 7a in Methanol



erythro

X	registry no.	temp, °C	$k \times 10^4$, s^{-1}
p-CH_3O, m-Br	66482-02-8	0.0	0.0836 ± 0.010
		32.73	16.7 ± 0.2
p-CH_3	66482-03-9	0.0	0.00917 ± 0.00003
		32.73	2.86 ± 0.04
H	66482-04-0	32.73	1.31 ± 0.02
		49.85	13.5 ± 0.5
p-Cl	66482-05-1	32.73	1.11 ± 0.01
		49.85	12.5 ± 0.1
p-NO_2	66482-07-3	32.73	0.362 ± 0.002
		49.85	5.22 ± 0.07

Anal. Calcd for $C_{11}H_{11}Br_2O_2$: C, 39.34; H, 3.57. Found: C, 39.40; H, 3.68.

The p-Cl acid was prepared by B: mp 184–185 °C; MS (70 eV) *m/e* (formula; rel intensity) 357.8649 ($C_{10}H_9{}^{79}Br^{81}Br^{37}ClO_2$ and $C_{10}H_9{}^{81}Br_2{}^{35}ClO_2$, 0.9), 355.8655 ($C_{10}H_9{}^{79}Br_2{}^{37}ClO_2$, and $C_{10}H_9{}^{79}Br^{81}Br^{35}ClO_2$, 1.4), 277 (16.8), 276 (12), 201 (62.3), 198 (47.6), 181 (47.1), 130 (77.9), 127 (75.9), 113 (84.7), and 111 (100).

The p-NO_2 acid was also prepared by B in 86% yield: mp 179–180 °C; MS (70 eV) *m/e* (formula, rel intensity) 287.9692 ($C_{10}H_9{}^{81}BrNO_4$, 26.7), 285.9727 ($C_{10}H_9{}^{79}BrNO_4$, 27.9), 207.0539 ($C_{10}H_9NO_4$, 75.4), 206.0450 ($C_{10}H_8NO_4$, 35.5), 190 (52), 162 (41.3), 161 (86.4), 160 (56.2), 116 (90), 115 (100).

The threo unsubstituted dibromo acid was available from another study, mp 108.5–109.5 °C.

Procedure for Kinetics. The requisite amount of 0.0966 N methoxide was added to a 50-mL volumetric flask and this was filled nearly to the calibration mark with pure methanol. The flask was thermostated. The weighed amount of 7 (equivalent to the methoxide concentration) was added as a solid and the total volume was adjusted to 50 mL. Aliquots were withdrawn at intervals. These were acidified and extracted twice with ether. The ether layer was extracted twice with water and the combined aqueous layers were assayed for bromide by titration with thiosulfate. Rates were run in duplicate. Table VI lists the data obtained.

Procedure for the Bromodecarboxylations. A weighed amount of the cinnamic acid (usually 250 mg) was placed in 20 mL of redistilled water. In early runs, two standards were used, p-toluic acid and hexamethylbenzene. Weighed quantities of each were placed in the reaction flask, along with a quantity of sodium carbonate equimolar to the two acids. A solution of 30 g of bromine in 100 mL of carbon tetrachloride was prepared, and 1 mL of this was added to the reaction flask. The flask was stirred vigorously until colorless and then worked up immediately. The aqueous solution was diluted to 100 mL and extracted twice with carbon tetrachloride. In early runs, this fraction was assayed separately. In later runs, the aqueous solution was acidified to pH 1 and extracted with methylene chloride and then with ether. The combined organic extracts were washed with water, dried ($MgSO_4$), evaporated, and assayed by NMR. Integration over the resonance in question vs. integration over the standard gave a molar ratio relative to the standard, from which a yield could be calculated using the known weight of the standard.

In runs using methanol, sufficient standard methoxide solution was added to neutralize the acids and the solution was made up to 20 mL with pure methanol. It was clear that the mass balances in methanol always were close to 100% so in later runs the standard was omitted, since its resonance interfered with other absorptions. Figure 1 shows the NMR spectrum of a typical reaction product and the assignment of peaks.

NMR assays of reaction products were run on A60-D and XL-100 instruments with product percentages determined from the average of 2–5 integrations over the characteristic resonances of the products.

Approximately 170 runs were made under various conditions, but only those using the procedure given earlier are reported. With X = p-CH_3O and CH_3, the mass balance was always very good (90% or above). With electron-withdrawing groups, the mass balance was poorer, but only those runs with a mass balance of 80% or greater are reported. The trends of the product yields in the runs not reported are quite similar to the ones reported.

Table VII. NMR Assignments (ppm) for the Products of Reaction[a]

compd	CH_3	CH
trans-**1a**	2.15	7.87
cis-**1a**	2.07	6.78
cis-**4a**	2.43	6.89
trans-**4a**[c]	2.47	6.62
cis-**5a**	1.49	5.80
trans-**5a**[c]	2.16	5.61
erythro-**6a**, OR′ = OCH_3	1.72	4.92
erythro-**6a**,[c] OR′ = OCH_3	1.67	
threo-**6a**,[c] OR′ = OCH_3	1.71	4.68
erythro-**6a**, OR′ = OH	1.73	5.36
erythro-**7a**	2.10	5.84
threo-**7a**[c]	1.88	5.83
8a	1.26	4.24
10a	2.68	5.38
11a	2.35	5.42
12a	1.37	5.23
13a	2.13	

compd	H	H′	$J_{HH'}$, Hz
1b	6.33	7.70	16
4b	6.62	6.97	14.5
trans-**5b**[b,d] (trans)	4.86	5.41	3.8
erythro-**6b**, OR′ = OCH_3	4.28	4.61	9.5
erythro-**6b**, OR′ = OH	4.44	5.04	variable
8b	3.52	4.13	1.7
9	3.67		
10b[e]	5.25	5.98	7
11b,[d] OR′ = OCH_3	5.03	5.81	5.5
11b, OR′ = OH[e]	4.96	5.72	5.5

[a] $COCl_3$ as solvent, unless otherwise specified. [b] CCl_4 as solvent. [c] CH_3OH as solvent. [d] X = H. [e] X = CH_3.

Product Identification. Products were identified by isolation and study by spectroscopic means, by synthesis by known methods, and in certain cases by study of the response of the material in question to reactions known to be characteristic of a certain structure. The NMR assignments are listed in Table VII, for X = p-Cl substituted substrates and products, in the solvents indicated.[41] Other substituents will give slightly different shifts.

Compound 4 appeared in the "neutral" extraction fraction during workup. For **4a**, the distinctive NMR doublet for methyl and multiplet for vinyl H were unmistakable. In one case (X = p-NO_2), the trans isomer was isolated: mp 85.5–86.5 °C; NMR (CCl_4) δ 2.52 (d, 3, J = 1.5 Hz, CH_3), 6.78 (m, 1, CH=C), 7.66 (d, 2, J = 9 Hz, Ar), and 8.14 (d, 2, J = 9 Hz, Ar).

Anal. Calcd for $C_9H_8BrNO_2$: C, 44.19; H, 3.42. Found: C, 44.19; H, 3.23.

The cis isomer (X = p-NO_2) showed the following NMR parameters: δ 2.46 (d, 3, J = 1.6 Hz, CH_3), 6.63 (m, 1, CHC), 7.07 (d, 2, J = 8 Hz, Ar), and 7.39 (d, 2, J = 8 Hz, Ar).

For **4b**, the NMR coupling constants were quite distinctive and clearly showed the state of isomerism.

The lactone **5a** also appeared in the neutral extraction fraction. This material was quite sensitive to acid, and especially to base, giving hydrolysis products. If stirred in water, **4** was also formed. The isolation of the lactone was attempted from the silver acetate catalyzed reaction, which formed a high level of lactone. A material of mp 76–78 °C was indeed obtained, but it was difficult to purify. The coupling constants for **5b** clearly indicate the state of isomerism (Table VII). The mode of formation of **5a** (both isomers) from the diastereomers of **7a** provides a strong indication of the state of isomerism.

The bromo ethers **6** appeared in the acid extraction fraction. The presence of CH_3, CH_3O, and CH was unmistakable from the NMR spectrum. In the case of **6b**, authentic materials (both diastereomers) were available from another study for comparison purposes. The bromohydrins **6a** and **6b** on treatment with base formed the epoxide

8, which was very sensitive to acid, in turn forming 9 and other materials.

Products 10 and 11 appeared in the neutral extraction fraction. These were also formed by the addition of bromine to 4 studied as a separate reaction. In the case of chlorination of **1b**, which is similar to bromination, the chloride analogues of 4 (7%), 11 (5%), and 10 (88%) were analyzed by VPC (Carbowax 20M, 0.1% on glass beads; flow 50 cm^3/min; column temperature 175 °C) with retention times of 1.7, 9.8, and 4.7 min, respectively. The first and third peaks were collected: NMR of 10 (CCl_4) δ 5.97 (d, 1, J = 6 Hz, PhC**H**Cl), 5.24 (d, 1, $CHCl_2$), and 7.4 (s, 5, Ph).

The structure of 12 appeared evident in the case of the reaction of **7a** (X = p-NO_2), where this was the predominant product in reactions run in Me_2SO–CH_3OH. This material was isolated for X = p-Cl for the reaction of **1a** with silver acetate. The structure of 13 was assigned as indicated in earlier discussion.

Acknowledgment. The funds for purchase of Varian XL-100 were partially supplied by NSF Grant GP-10293, which is gratefully acknowledged.

Registry No.—*cis*-**1a** (X = p-CH_3O), 66482-31-3; *trans*-**1a** (X = p-CH_3O), 66482-32-4; *cis*-**1a** (X = p-CH_3O) acid, 13048-81-2; *trans*-**1a** (X = p-CH_3O) acid, 13048-80-1; *cis*-**1a** (X = p-CH_3), 66482-33-5; *trans*-**1a** (X = p-CH_3), 66482-34-6; *cis*-**1a** (X = p-CH_3) acid, 66482-35-7; *trans*-**1a** (X = p-CH_3) acid, 32655-80-4; *cis*-**1a** (X = H), 66482-36-8; *trans*-**1a** (X = H), 66482-37-9; *cis*-**1a** (X = H) acid, 15250-29-0; *trans*-**1a** (X = H) acid, 1895-97-2; *cis*-**1a** (X = p-Cl), 66482-38-0; *trans*-**1a** (X = p-Cl), 66482-39-1; *cis*-**1a** (X = p-Cl) acid, 66482-40-4; *trans*-**1a** (X = p-Cl) acid, 14328-88-2; *cis*-**1a** (X = o-Cl), 66482-41-5; *trans*-**1a** (X = o-Cl), 66482-42-6; *cis*-**1a** (X = o-Cl) acid, 66482-43-7; *trans*-**1a** (X = o-Cl) acid, 66482-44-8; *cis*-1a (X = p-NO_2), 66482-45-9; *trans*-**1a** (X = p-NO_2), 66482-46-0; *cis*-**1a** (X = p-NO_2) acid, 13048-76-5; *trans*-**1a** (X = p-NO_2) acid, 13048-77-6; *cis*-**1b** (X = p-CH_3O), 66482-12-0; *trans*-**1b** (X = p-CH_3O), 66482-13-1; *cis*-**1b** (X = p-CH_3O) acid, 5676-64-2; *trans*-**1b** (X = p-CH_3O) acid, 943-89-5; *cis*-**1b** (X = o-CH_3O), 66482-14-2; *trans*-**1b** (X = o-CH_3O), 66482-15-3; *cis*-**1b** (X = o-CH_3O) acid, 14737-91-8; *trans*-**1b** (X = o-CH_3O) acid, 1011-54-7; *cis*-**1b** (X = H), 66482-16-4; *trans*-**1b** (X = H), 17263-38-6; *cis*-**1b** (X = H) acid, 102-94-3; *trans*-**1b** (X = H) acid, 140-10-3; *cis*-**1b** (X = p-CH_3), 66482-17-5; *trans*-**1b** (X = p-CH_3), 66482-18-6; *cis*-**1b** (X = p-CH_3) acid, 14290-88-1; *trans*-**1b** (X = p-CH_3) acid, 940-61-4; *cis*-**1b** (X = o-Cl), 66482-19-7; *trans*-**1b** (X = o-Cl), 66482-20-0; *cis*-**1b** (X = o-Cl) acid, 704-96-1; *trans*-**1b** (X = o-Cl) acid, 939-58-2; *cis*-**1b** (X = m-NO_2), 66482-21-1; *trans*-**1b** (X = m-NO_2), 66482-22-2; *cis*-**1b** (X = m-NO_2) acid, 5676-61-9; *trans*-**1b** (X = m-NO_2) acid, 1772-76-5; *cis*-**1b** (X = p-NO_2), 66482-23-3; *trans*-**1b** (X = p-NO_2), 66482-24-4; *cis*-**1b** (X = p-NO_2) acid, 14290-91-6; *trans*-**1b** (X = p-NO_2) acid, 882-06-4; *cis*-**1b** (X = p-Cl), 66482-25-5; *trans*-**1b** (X = p-Cl), 66482-26-6; *cis*-**1b** (X = p-Cl) acid, 5676-62-0; *trans*-**1b** (X = p-Cl) acid, 940-62-5; *cis*-**4a** (X = p-Cl), 66482-27-7; *trans*-**4a** (X = p-Cl), 66482-28-8; *cis*-**4b** (X = p-Cl), 66482-29-9; *trans*-**4b** (X = p-Cl), 66482-30-2; *cis*-**4a** (X = p-NO_2), 38319-07-2; *trans*-**4a** (X = p-NO_2), 38319-08-3; *cis*-**5a** (X = p-Cl), 66481-94-5; *trans*-**5a** (X = p-Cl), 66481-95-6; *trans*-**5b** (X = H), 66481-96-7; *erythro*-**6a** (X = p-Cl; R′ = CH_3), 66481-97-8; *threo*-**6a** (X = p-Cl; R′ = CH_3), 66481-98-9; *erythro*-**6a** (X = p-Cl; R′ = H), 66481-99-0; *erythro*-**6b** (X = p-Cl; R′ = CH_3), 66482-00-6; *erythro*-**6b** (X = p-Cl; R′ = H), 66482-01-7; *threo*-**7a** (X = p-Cl), 66482-06-2; *erythro*-**7a** (X = 4MeO,3-Br) acid, 66482-08-4; *erythro*-**7a** (X = p-CH_3) acid, 66482-09-5; *erythro*-**7a** (X = H) acid, 66482-10-8; *erythro*-**7a** (X = p-Cl) acid, 66482-11-9; *erythro*-**7a** (X = p-NO_2) acid, 66481-86-5; **8a** (X = p-Cl), 66481-87-6; **8b** (X = p-Cl), 66481-88-7; **9** (X = p-Cl), 4251-65-4; **10a** (X = p-Cl), 66481-89-8; **10b** (X = p-CH_3), 66481-90-1; **11b** (R′ = CH_3; X = H), 52809-81-1; **11b** (R′ = H; X = p-CH_3), 66481-91-2; **12a** (X = p-Cl), 66481-92-3; **13a** (X = p-Cl), 66481-93-4.

References and Notes

(1) (a) J. March, "Advanced Organic Chemistry, Reactions, Mechanism and Structure", 2nd ed, McGraw-Hill, New York, N.Y., 1977, p 672, 680, and references cited herein; (b) p 253.
(2) G. A. Olah and P. Schleyer, "Carbonium Ions", Vol. II, Wiley-Interscience, New York, N.Y., 1970.
(3) (a) N. Hanson and T. James, *J. Chem. Soc.*, 1955, 2979 (1928); (b) H. Robinson and T. James, *ibid.*, 1454 (1933); (c) S. DeYoung, S. Ehrlich, and E. Berliner, *J. Am. Chem. Soc.*, **99**, 290 (1977).
(4) D. S. Tarbell and P. D. Bartlett, *J. Am. Chem. Soc.*, **59**, 407 (1937).
(5) J. D. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5974 (1957).
(6) (a) M. C. Cabaleiro and M. D. Johnson, *Chem. Commun.*, 454 (1965); (b) M. C. Cabaleiro, M. D. Johnson, and N. Swedlund, *J. Chem. Soc. B*, 1022 (1967); (c) M. D. Johnson and E. N. Trachtenberg, *ibid.*, 1018 (1968); (d) see also J. Read and A. Andrews, *ibid.*, **119**, 1774 (1921); (e) J. Agoff and M. C. Cabaleiro, *Tetrahedron Lett.*, 3535 (1975).
(7) In our hands, β-lactone can be observed by IR upon treatment of the anions of α-phenylcinnamate and *trans*-cinnamate acid with bromine and chlorine, respectively.
(8) C. A. Kingsbury, *J. Org. Chem.*, **33**, 3247 (1968).
(9) (a) H. T. Liang and P. D. Bartlett, *J. Am. Chem. Soc.*, **80**, 3585 (1958); (b) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966); (c) W. Barnett and J. C. McKenna, *Chem. Commun.*, 551 (1971); (d) W. Adam, J. Baeza, and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2000 (1972); (e) H. E. Zaugg, *Org. React.*, **8**, 305 (1954), reviews the reactions of β-lactones; (f) G. Blackburn and H. Dodds, *J. Chem. Soc., Perkin Trans. 2*, 377 (1972).
(10) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 328; (b) W. R. Vaughan, R. Cayle, J. Csapilla, and P. Scheiner, *J. Am. Chem. Soc.*, **87**, 2204 (1965).
(11) The elusive α-lactone has now been characterized: O. L. Chapman, P. Wojtkowski, W. Adam, O. Rodriguez, and R. Ruckstand, *J. Am. Chem. Soc.*, **94**, 1365 (1972). It was stated that the zwitterionic and covalent forms were in equilibrium.
(12) (a) In addition, bromide converts bromine partially to tribromide and may alter the nature of the brominating agent, F. R. Jensen and D. D. David, *J. Am. Chem. Soc.*, **93**, 4049 (1971). (b) J. H. Ralston and K. Yates, *ibid.*, **94**, 1403 (1972), showed that Br_3^- additions are characterized by lower Hammett ρ values than molecular bromine additions.
(13) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4025 (1955).
(14) For a different possible route to epoxide see S. J. Cristol and W. Norris, *J. Am. Chem. Soc.*, **75**, 632, 2645 (1953).
(15) (a) P. I. Abell, *J. Am. Chem. Soc.*, **88**, 1346 (1966); (b) D. S. Noyce, P. King, F. Kirby, and W. Reed, *ibid.*, **84**, 1632 (1962).
(16) (a) R. C. Fahey and H.-J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968), believe that addition of bromine to 1-phenylpropenes essentially involves open benzylic ions, although the tendency for bridged ions is greater than in the case of chlorination (M. L. Poutsma, *ibid.*, **87**, 4285 (1965)). (b) K. Yates and W. Wright, *Can. J. Chem.*, **45**, 167 (1967), show that Hammet's ρ for addition is rather small and conclude the intermediate is probably bridged. (c) J. Dubois and G. Barbier, *Tetrahedron Lett.*, 1217 (1965), favor a bridged ion where electron-withdrawing aromatic substituents are present but an open ion where electron donating substituents are present. (d) J. Ralston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969) present evidence for an open ion; K. Yates and R. S. McDonald, *ibid.*, **93**, 6297 (1971). (e) M. F. Ruasse and J. Dubois, *ibid.*, **97**, 1977 (1975), again prefer an interpretation involving bridged bromonium ions. (f) G. Olah and T. Hockswender, *ibid.*, **96**, 3574 (1974), emphasize the importance of a π complex between olefin and bromine (cf. also ref 16a). See also: C. G. Gebelin and G. D. Frederick, *J. Org. Chem.*, **37**, 2211 (1972). (g) See also: V. Seth and A. Bose, *J. Indian Chem. Soc.*, **48**, 575 (1971), and A. Gzoszkowski and J. Sienkiewicz, *Rocz. Chem.*, **45**, 1779 (1971).
(17) For a related complex scheme for halogenation, see H. Kwart and F. Scalzi, *J. Am. Chem. Soc.*, **86**, 5496 (1964).
(18) L. A. Singer and N. Kong, *J. Am. Chem. Soc.*, **89**, 6805 (1967).
(19) (a) J. Hine, *J. Am. Chem. Soc.*, **88**, 5525 (1966), and related papers; (b) O. S. Tee, *ibid.*, **91**, 7144 (1969); O. S. Tee and K. Yates, *ibid.*, **94**, 3072 (1972); (c) S. Ehrenson, *ibid.*, **96**, 3778 (1974); **96**, 3784 (1974); (d) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry", Oxford University Press, London, 1949, pp 104 and 114.
(20) The possibility exists that the system possesses enough energy at the first transition state to carry it over the second, without collisional deactivation and subsequent reactivation. Thus, product formation could occur within a very few vibrations, and thus be operationally concerted. This is essentially a "hot ion" explanation which, in general, is not well regarded by the scientific community. For most recent criticism, see R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976). However, P. Beak, *Acc. Chem. Res.*, **9**, 230 (1976), favorably considers similar highly reactive intermediates. C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **85**, 2519 (1963), have shown that highly energetic ions may react in a stereospecific manner.
(21) Carbonium ions resulting from additions to alkenes generally show slightly different reactions compared to carbonium ions generated by solvolysis: H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.*, **86**, 466, 3898, 3900 (1964). Subtle differences of a "memory" nature remain to be explained.
(22) E. Trumbull, T. Finn, K. Ibne-Rasa, and C. Sauers, *J. Org. Chem.*, **27**, 2339 (1962).
(23) (a) E. Grovenstein and D. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); (b) K. Ibne-Rasa and A. Ahmad, *J. Sci. Res. (Lahore)*, **3**, 1 (1968).
(24) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 295 (1970); **35**, 299 (1970).
(25) The stereochemical data given in ref 22 are regarded in ref 24 as inconclusive due to the fact that known reactions proceeding through zwitterions are stereospecific, namely the cleavage of β-lactones (possibly also a least motion process). However, Noyce and Brauman report that zwitterions derived from unstrained open chain substrates, namely hydroxy carboxylates, rather similar to **7**, react to give the most stable olefin after various types of internal rotation (cf. D. S. Noyce and S. Brauman, *J. Am. Chem. Soc.*, **90**, 5218 (1968)). See, however, ref 9b.
(26) A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962); also ref 27, pp 81 and 93.
(27) W. H. Saunders and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New York, N.Y., 1973, pp 71–89.
(28) M. H. O'Leary, D. Richards, and D. Hendrickson, *J. Am. Chem. Soc.*, **92**, 4435 (1970).
(29) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Longmans, Green and Co., New York, N.Y., 1956, pp 708 and 711.
(30) W. H. Perkin, *J. Chem. Soc.*, **31**, 412 (1877).
(31) K. von Auwers, *Justus Liebigs Ann. Chem.*, **227**, 485 (1885).
(32) H. Erdman, *Justus Liebigs Am. Chem.*, **227**, 247 (1885).
(33) W. J. Gensler and E. Berman, *J. Am. Chem. Soc.*, **80**, 4949 (1958).
(34) J. van der Lee, *Recl. Trav. Chim. Pays-Bas*, **45**, 674 (1926).

(35) T. Posner, *J. Prakt. Chem.*, **82**, 425 (1910).
(36) T. Posner and G. Schreiber, *Chem. Ber.*, **57**, 1127 (1924).
(37) K. von Auwers, *Justus Liebigs Ann. Chem.*, **422**, 133 (1920).
(38) F. Tiemann and J. Oppermann, *Chem. Ber.*, **13**, 2059 (1880).
(39) J. J. Sudborough, *J. Chem. Soc.*, 666 (1903).
(40) R. Stoermer and P. Heymann, *Chem. Ber.*, **44**, 637 (1911).
(41) T. Wittstruck and G. N. Trachtenberg, *J. Am. Chem. Soc.*, **89**, 3802 (1967).

Comparison of the Addition of Bromine Chloride to 1-Hexene and 1-Hexyne in Carbon Tetrachloride and Methanol

Victor L. Heasley,* Dale F. Shellhamer, John A. Iskikian, and David L. Street

Department of Chemistry, Point Loma College, San Diego, California 92106

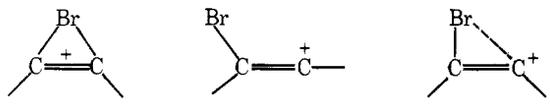
Gene E. Heasley

Department of Chemistry, Bethany Nazarene College, Bethany, Oklahoma 73008

Received January 26, 1978

Addition of bromine chloride (BrCl) to 1-hexene in CCl_4 gives a 61:39 ratio of Markownikoff to anti-Markownikoff products (1-bromo-2-chlorohexane to 1-chloro-2-bromohexane), suggesting a symmetrically bridged bromonium ion intermediate in this reaction. 1-Hexyne reacts with BrCl to give Markownikoff and anti-Markownikoff products in the ratio of 90:10 (*trans*-1-bromo-2-chloro-1-hexene/*trans*-1-chloro-2-bromo-1-hexene). These data, together with the fact that the alkene products have trans stereochemistry, implicate a weakly bridged bromonium in the addition of BrCl to 1-hexyne. The bromochlorohexanes were analyzed by mass specrometry, and ^{13}C NMR analyses distinguished between the bromochlorohexenes. In CH_3OH, 1-hexyne and BrCl give only Markownikoff bromochloride (trans isomer) and 1,1-dibromo-2-hexanone. (The result of two additions of Br, OCH_3, followed by hydrolysis of the intermediate ketal.) Markownikoff and trans additions suggest that a weakly bridged bromonium ion, rather than a vinyl cation, is involved. Addition of BrCl to 1-hexene in CH_3OH gives the following ratios of Markownikoff to anti-Markownikoff bromochlorides and methoxy bromides: 25:24 and 34:17.

A few years ago, Pincock and Yates[1] suggested that the intermediate involved in the bromination of some alkylacetylenes in acetic acid is a bridged bromonium ion (**1a**) and not an open vinyl cation (**1b**). They based their conclusion on the assumption that an unbridged vinyl cation should give some *cis*-1,2-dibromide; only *trans*-1,2-dibromide was reported.[2] More recently, Olah and Hochswender[3] drew the same conclusion from their studies of the bromination of 1-hexyne in 1,1,2-trichlorotrifluoroethane. Neither study, however, permitted a conclusion to be drawn concerning the symmetry of the bridging in the bromonium ion. Conceivably a weakly bridged ion such as **1c** is involved, but with sufficient bridging to prevent syn addition.

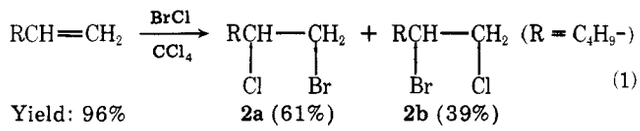


1a **1b** **1c**

We proposed to study the addition of bromine chloride (BrCl) to both 1-hexene and 1-hexyne in a nonpolar solvent (CCl_4) and a polar solvent (CH_3OH). Our initial assumption was that the extent of anti-Markownikoff ring opening of either the saturated bromonium ion from 1-hexene or the unsaturated ion from 1-hexyne should be significant if the bridging is symmetrical and decrease to zero with a carbocation. Although Pincock and Yates[1] did not observe solvent incorporation when 1-hexyne was brominated in acetic acid, we suspected that ring opening of the intermediate bromonium ions would occur in the more nucleophilic solvent methanol. Solvent incorporation is a predominant reaction in the bromination of 1-hexene in methanol.[4,5]

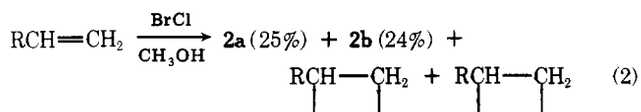
Results

Products from the addition of BrCl to 1-hexene in CCl_4 and CH_3OH under ionic conditions are shown in eq 1 and 2.



$$RCH{=}CH_2 \xrightarrow[CCl_4]{BrCl} \underset{Cl\ \ Br}{RCH{-}CH_2} + \underset{Br\ \ Cl}{RCH{-}CH_2} \quad (R = C_4H_9\text{-}) \qquad (1)$$

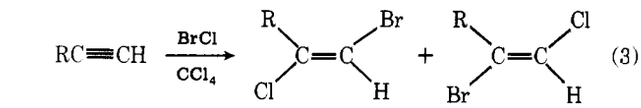
Yield: 96% **2a** (61%) **2b** (39%)



$$RCH{=}CH_2 \xrightarrow[CH_3OH]{BrCl} \mathbf{2a}\,(25\%) + \mathbf{2b}\,(24\%) + \underset{H_3CO\ \ Br}{RCH{-}CH_2} + \underset{Br\ \ OCH_3}{RCH{-}CH_2} \qquad (2)$$

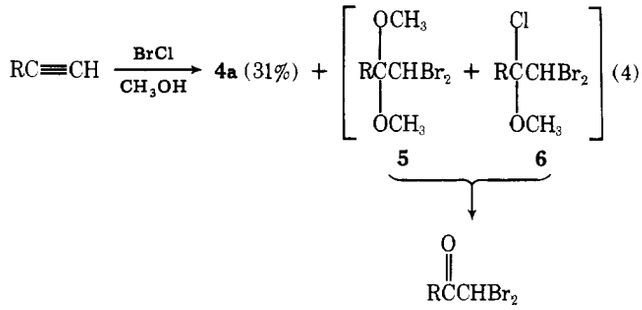
Yield: 84% **3a** (34%) **3b** (17%)

1-Hexyne and BrCl under ionic conditions gave the products shown in eq 3 and 4. We postulate that **5** and **6** are involved and that they result from addition to **8**, because **8** is more reactive than the starting 1-hexyne (eq 5). 2,2-Dibromohexanal (**9**) was not detected, indicating that anti-Markownikoff addition of Br, OCH_3 did not occur (eq 6).



$$RC{\equiv}CH \xrightarrow[CCl_4]{BrCl} \underset{Cl\ \ H}{\overset{R}{\overset{|}{C}}{=}\overset{Br}{\overset{|}{C}}} + \underset{Br\ \ H}{\overset{R}{\overset{|}{C}}{=}\overset{Cl}{\overset{|}{C}}} \qquad (3)$$

Yield: 79% **4a** (90%) **4b** (10%)



$$RC{\equiv}CH \xrightarrow[CH_3OH]{BrCl} \mathbf{4a}\,(31\%) + \left[\underset{OCH_3}{\overset{OCH_3}{\overset{|}{R}CCHBr_2}} + \underset{OCH_3}{\overset{Cl}{\overset{|}{R}CCHBr_2}}\right] \qquad (4)$$

5 **6**

$$\underset{\|}{\overset{O}{\overset{|}{RCCHBr_2}}}$$

7 (69%)