Mechanisms of Addition. Part II.[1] The Stereochemistry of Addition of Bromine and Bromine Acetate to Some Phenyl-substituted Olefins

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The addition of bromine acetate to some phenyl-substituted olefins is more stereospecific than the corresponding additions of chlorine acetate. The stereochemistry of addition of bromine to methyl *para*-methyl-*trans*-cinnamate depends on concentration. The results have mechanistic implications.

THE pathway by which bromine adds to olefinic substances has been investigated and reviewed [2-7] extensively. Both kinetic processes which are second order in bromine and first order in bromine have been studied [2-7] and it has been suggested that in some cases these reactions proceed through a common intermediate [8] because they respond similarly to substituent effects and produce similar ratios of products. However, some warning has been given that the pathway for a particular olefin must be treated on its own merit; [2,9,10] indeed a number of processes may be available by which bromine and other halogens add to double bonds. Williams [2] warned, ' Far from being an automatic trap for unwary halogen, the double bond is rather an objective to be sprung only by subtle and devious attack '.

We have investigated the reactions of some phenyl-substituted olefins with molecular bromine using substituent effects and bromine acetate (sometimes called acetyl hypobromite) as tools to elucidate mechanism, as we have recently done for molecular chlorine.[11] The results extend those of a preliminary communication;[1] they throw new light on the mechanism of addition of bromine and establish some aspects of the mechanism of addition of bromine acetate.

RESULTS AND EXPERIMENTAL

Acetic acid was commercial material analytical grade, re-distilled, m.p. 16.4—16.6°. Other solvents were also analytical grade. Substituted cinnamic acid derivatives were prepared as described previously.[11] 1-Phenylpropene was commercial material with physical properties as described by others.[12] I.r. spectra were recorded using a Perkin-Elmer 237 grating spectrometer, and ^{1}H n.m.r. spectra by a Varian T60 instrument. Microanalyses are by Dr A. D. Campbell and his staff, University of Otago, Dunedin. Mass spectra were run at 70—12 eV with a direct insertion probe, trap current 300 μA, and source temperature *ca.* 200°. Bromine was analytical grade and added to the reaction mixtures in one of the manners described below. Bromine acetate was prepared in carbon tetrachloride [13,14] from silver acetate using a very slight excess of silver acetate. It was filtered from the precipitated silver bromide before use,[13] and standardised with sodium thiosulphate and potassium iodide. Concentrated solutions were brown to straw coloured, unlike the red-brown colour of molecular bromine but similar in colour to concentrated solutions of chlorine acetate.[15] Bromine acetate was added to the reaction mixtures in one of the manners described below.

Several methods of mixing of reagent and work up of reaction mixtures were employed. In method (A) bromine or bromine acetate was added neat or in concentrated solution in order to model common synthetic procedures. In method (B), the olefin was dissolved in half the total volume of solvent and the electrophile dissolved in an equal volume. This ensured that localised high concentrations of electrophile were not obtained. On work up several methods were employed. In Method (C) the solvent together with any volatile material was removed by evaporation at low pressure. In methods (D) and (E) the reaction mixture was poured into water and extracted with sufficient volumes of diethyl ether or chloroform. Acetic acid and any added electrolytes were removed by washing with water in method (D), but with saturated aqueous sodium hydrogen carbonate solution in method (E). Because bromine acetate was prepared in carbon tetrachloride solution some experiments contained 5% CCl_4 [method (F)]. In method (G) chloroform was used as solvent instead of acetic acid.

In analysing the reaction mixtures ^{1}H n.m.r. spectroscopy was used. The relative areas of the signals of the methoxycarbonyl groups were used where applicable, and the acetoxy-signals were also used to calculate product ratios. A third estimation was available for some experiments from 2- and 3-H for the cinnamate derivatives or from the methyl protons of 1-phenyl propene derivatives. These methods gave similar results for most of the experiments performed. Where there were some small differences the average values obtained by the various methods were taken. The ^{1}H n.m.r. signals of the various derivatives are listed in Tables 1 and 2 and the product ratios from the additions studied under the various conditions are listed in Table 3.

The four possible racemic bromohydrins (1 and 2; R^1 =

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[9] F. Garnier and J. E. Dubois, *Bull. Soc. chim. France*, 1968, 3797.
[10] P. B. D. de la Mare and B. N. B. Hannan, *J.C.S. Perkin II*, 1973, 1086.
[11] P. B. D de la Mare, M. A. Wilson, and M. J. Rosser, *J.C.S. Perkin II*, 1973, 1480.
[12] R. C. Fahey and H.-J. Schneider, *J. Amer. Chem. Soc.*, 1968, **90**, 4429; J. H. Rolston and K. Yates, *ibid.*, 1969, **91**, 1469, 1477, 1483.
[13] V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.*, 1972, **37**, 2228.
[14] H. Haubenstock and C. A. Van der Werf, *J. Org. Chem.*, 1964, **29**, 2993.
[15] M. A. Wilson, Ph.D. Thesis, University of Auckland, 1974.

TABLE 1

^{1}H N.m.r. spectra of derivatives $R^3C_6H_4CH(OR^1)CHBrCO_2R^2$, of 3-aryl-2-bromo-3-hydroxypropionic acid

Isomer, see formulae (1) and (2)	R^1	R^2	R^3	Chemical shifts (τ) ($CDCl_3$) 3-H	2-H	Me(R^1)	Me(R^2)	Me(R^3)	Coupling constants $J_{2,3}$/Hz
erythro	Ac	Me	*p*-OMe	3.9	5.45	8.0	6.2	6.2	10
threo or *erythro*	H	Me	*p*-OMe	5.05	5.7		6.3	6.3	9
erythro	Ac	Me	*p*-Me	3.85	5.45	8.0	6.2	7.65	10
threo	Ac	Me	*p*-Me	3.8	5.55	7.9	6.4		9
erythro	Ac	Me	*p*-H	3.8	5.45	8.05	6.25		9.8
threo	Ac	Me	*p*-H	3.75	5.45	7.9	6.4		9.2
erythro	H	Me	*p*-H	5.0	5.7		6.35		9
erythro	Ac	Me	*p*-Cl	3.85	5.5	8.0	6.2		9.7
threo	Ac	Me	*p*-Cl	3.8	5.55	7.9	6.35		

TABLE 2

^{1}H N.m.r. spectra of derivatives $R^3C_6H_4CHBrCHBrCO_2R^2$ of 3-aryl-2,3-dibromopropionic acid

Isomer, see formulae (3) and (4)	R^2	R^3	Chemical shifts τ ($CDCl_3$) 3-H	2-H	Me(R^2)	Me(R^3)	Coupling constants $J_{2,3}$/Hz
erythro	Me	*p*-OMe	4.6	5.15	6.1	6.2	12.0
threo	Me	*p*-OMe	4.7	5.3	6.45		10.4
erythro	Me	*p*-Me	4.6	5.15	6.15	7.65	11.6
threo	Me	*p*-Me	4.7	5.25	6.45	7.65	10.0
erythro[a]	Me	*p*-H	4.6	5.1	6.15		12
threo[a]	Me	*p*-H	4.65	5.15	6.5		10
erythro	Me	*p*-Cl	4.6	5.1	6.15		11.8
threo	Me	*p*-Cl	4.65	5.2	6.45		10
erythro	Me	*p*-NO_2	4.55	5.1	6.05		12.2

[a] Lit.,[18] τ(CCl_4) (*erythro*- and *threo*-mixture) 4.68—5.35 (4d, J 10 and 12 Hz), 6.12 (s), and 6.50 (s).

TABLE 3

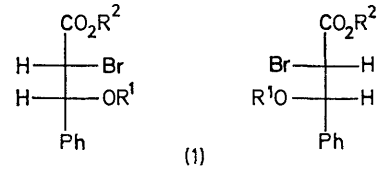
Product proportions and ratios of *trans* : *cis* addition for the reaction of bromine acetate and bromine with some methyl *trans*-cinnamates ($R^3C_6H_4CH{=}CHCO_2Me$) in acetic acid at 25°

R^3	[Olefin]/M	[Electrophile]/M	Reaction (%)	Experimental procedure	*erythro* Acetoxybromides	*threo* Acetoxybromides	*erythro* Dibromides	*threo* Dibromides	*anti* : *syn* Acetoxybromides	*anti* : *syn* Dibromides
p-OMe	10^{-2}	BrOAc 10^{-2}	—	A, D, F	100	—	—	—	Large	—
p-OMe[a]	10^{-2}	Br_2 10^{-2}	—	A, C	21	—	72	7	Large	10.3
p-OMe[a,c]	10^{-3}	Br_2 10^{-3}	—	A, E	*ca.* 45	—	—	—	Large	—
p-OMe[a,c]	10^{-2}	Br_2 10^{-2}	—	A, E	*ca.* 24	—	—	—	Large	—
p-OMe	10^{-3}	Br_2 10^{-3}	—	B, C	3	—	84	13	i	6.5
p-OMe	10^{-3}	Br_2 10^{-3}	—	A, C	—	—	86	14	—	6.2
p-Me	10^{-2}	BrOAc 10^{-2}	90	A, D, F	90	10	—	—	9.0	—
p-Me	2.5×10^{-2}	BrOAc 2.5×10^{-2}	85	A, D, F	86	14	—	—	6.1	—
p-Me	10^{-3}	BrOAc 10^{-3}	85	A, D, F	86	14	—	—	6.1	—
p-Me[b]	10^{-1}	Br_2 0.24	100	A, E	5	—	70	25	i	2.8
p-Me[b]	5×10^{-2}	Br_2 0.18	100	A, E	9	—	69	22	i	3.1
p-Me[b]	2.5×10^{-2}	Br_2 0.25	100	A, E	10	—	76	14	i	5.4
p-Me[a,b,d]	2.5×10^{-2}	Br_2 0.25	100	A, E	48	—	52	—	Large	Large
p-Me	2.5×10^{-2}	Br_2 2.5×10^{-2}	71	B, D, F	15	—	53	32	Large	1.7
p-Me	10^{-2}	Br_2 2.5×10^{-2}	100	A, E	15	—	49	36	Large	1.4
p-Me	10^{-2}	Br_2 10^{-1}	100	A, E	18	—	51	31	Large	1.6
p-Me[f]	10^{-2}	Br_2 10^{-2}	63	B, D	49	—	39	12	Large	3.3
p-Me	10^{-2}	Br_2 10^{-2}	78	A, D	17	—	49	36	Large	1.4
p-Me	10^{-2}	Br_2 10^{-2}	50	B, C, G	—	—	82	18	—	4.5
p-Me[b]	10^{-3}	Br_2 10^{-2}	100	A, D	12	—	54	34	i	1.6
p-Me	5×10^{-3}	Br_2 5×10^{-3}	60	B, D	17	—	52	31	i	1.7
p-Me	2.5×10^{-3}	Br_2 2.5×10^{-3}	60	B, E	16	—	58	26	i	2.2
p-Me[b]	10^{-3}	Br_2 2×10^{-3}	100	B, D	—	—	92	8	—	11.5
p-Me	10^{-3}	Br_2 10^{-3}	66	B, E	7	—	84	9	i	9.3
p-Me	10^{-3}	Br_2 10^{-3}	66	B, D	7	—	84	9	i	9.3
p-Me	10^{-3}	Br_2 10^{-3}	60	B, D, F	4	—	89	7	i	12.7
p-Me	10^{-3}	Br_2 10^{-3}	44	B, D	7	—	71	22	i	3.2
p-Me	10^{-3}	Br_2 10^{-3}	66	A, D	10	—	86	4	i	Large
p-H	10^{-2}	BrOAc 10^{-2}	84	A, D, F	94	6	—	—	⩾10	—
p-H	10^{-2}	Br_2 10^{-1}	100	A, D	28	3	58	11	9.3	5.3
p-H	10^{-2}	Br_2 10^{-1}	100	A, D	30	4	59	7	7.5	8.4
p-H[e]	10^{-2}	Br_2 10^{-2}	—	—	*ca.* 25	—	*ca.* 75	—	Large	Large
p-Cl	10^{-2}	BrOAc 10^{-2}	78	A, D, F	90	10	—	—	9.0	—
p-Cl	10^{-2}	Br_2 10^{-1}	86	A, D	24	—	65	11	Large	5.9
p-NO_2	10^{-2}	Br_2 10^{-1}	82	A, D	—	—	100	—	—	>20

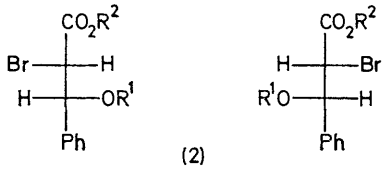
—, Not detected. i, indeterminate.

[a] Other products present. [b] Aromatic substitution also occurs. [c] Other products are bromohydrins. [d] +0.5M-NaOAc. [e] Values from ref. 18. [f] +1.0M-NaOAc.

R^2 = H) which could be formed by the addition of hypobromous acid to cinnamic acid have been described.[16] Under the conditions for which are recorded the addition of bromine acetate to methyl *trans*-cinnamate the only signals detected in the ^{1}H n.m.r. spectra of the products obtained from the reaction were those of the two racemates (1 and 2; R^1 = Ac, R^2 = Me). These compounds were synthesised independently from the parent hydroxy-acids (1 and 2; R^1 = R^2 = H) of known stereochemistry.[16]



(1)
(erythro)



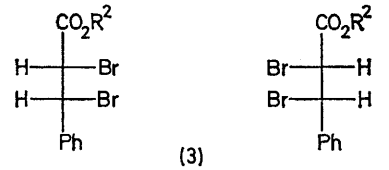
(2)
(threo)

Methyl erythro-3-*Acetoxy*-2-*bromo*-3-*phenylpropionate* (1; R^1 = Ac, R^2 = Me).—The acid (1; R^1 = R^2 = H) was prepared from the *trans*-cinnamic acid *via* the dibromide adduct [17] and had m.p. 126° (lit.,[16] 125°), $\nu_{max.}$ (Nujol; KBr) 3 400 (OH), 3 030—3 900, 1 720 (C=O), and 1 250 cm^{-1}. Its ^{1}H n.m.r. and mass spectrum have previously been described.[16] It was dissolved in excess of methanol containing a few drops of concentrated sulphuric acid and heated under reflux for 24 h. The product was dissolved in diethyl ether, washed with water and worked up in the normal manner, to give *methyl* erythro-2-*bromo*-3-*hydroxy*-3-*phenylpropionate* (1; R^1 = H, R^2 = Me), m.p. 62° (Found: C, 46.3; H, 3.9. $C_{10}H_{11}BrO_3$ requires C, 46.3; H, 4.2%), n.m.r. in Table 1, *m/e* 260, 258, 243, 241, 229, 227, 179, 162, 161, 154, 152, 131, and 106, $\nu_{max.}$ ($CHCl_3$) 3 600 (OH), 3 030, 3 010, 1 730 (C=O), 1 440, 1 275, 1 140, and 1 020 cm^{-1}. Treatment of the bromohydrin (1; R^1 = H, R^2 = Me) with acetic anhydride and a few drops of pyridine at room temperature for 24 h yielded after hydrolysis of the acetic anhydride with water, methyl *erythro*-3-acetoxy-2-bromo-3-phenylpropionate (1; R^1 = Ac, R^2 = Me) as an oil, n.m.r. in Table 1, *m/e* 302, 300, 271, 269, 260, 258, 243, 242, 241, 240, 223, 222, 221, 220, 211, 209, 180, 179, 178, 162, 161, and 149, $\nu_{max.}$ ($CHCl_3$) 3 030, 3 010, 1 760 (C=O), 1 740 (C=O), 1 440, 1 275, 1 140, and 1 020 cm^{-1}.

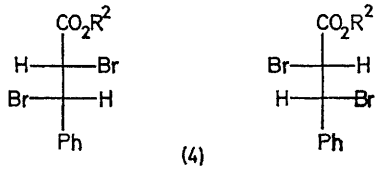
Methyl threo-3-*Acetoxy*-2-*bromo*-3-*phenylpropionate* (2; R^1 = Ac, R^2 = Me).—This derivative was prepared in an identical manner to the *erythro*-isomer but from the *threo*-hydroxy-acid (2; R^1 = H, R^2 = H) which was prepared from *cis*-cinnamic acid as described elsewhere.[16] Its ^{1}H n.m.r. spectrum is described in Table 1 and its mass spectrum was similar to the *erythro*-isomer.

The products from the substituted methyl cinnamates were not so fully characterised; there were no extraneous signals * unless otherwise noted, and they were assigned by virtue of the similarities in chemical shift and coupling constant. These values are listed in Tables 1 and 2. The products of addition initiated by molecular bromine (3 and 4; R^2 = Me) were assigned in a similar manner. The dibromide adducts of methyl cinnamate have been assigned previously by other workers [18] on the basis of the relative rates of base induced dehydrobromination.

For the products of addition to methyl *para*-methoxy-*trans*-cinnamate investigated, the dibromides were found to be hydrolysed to the bromohydrins when aqueous sodium hydrogen carbonate was used in the work up. At higher concentrations of electrophile there was some evidence from the splitting of the ArH protons in the region τ 2.0—3.3 in the ^{1}H n.m.r. spectrum of the product mixtures that some aromatic substitution had occurred. This was checked for some representative mixtures by mass spectrometry, giving molecular ions at *m/e* (434, 432, 430, 428), (354, 352, 350), (412, 410, 408), and (332, 330) corresponding to the 2,3,3′-tribromo-adduct, 2,3-dibromo-adduct, 2,3′-dibromo-3-acetoxy-adduct, and acetoxybromide. Similar experiments on the products of chlorine acetate addition to the methoxyolefin confirmed our conclusions regarding addition and subsequent aromatic substitution discussed elsewhere.[11] We were also able to show that in experiments with methyl *para*-methyl-*trans*-cinnamate aromatic substitution occurs to a small extent in those experiments in which excess of bromine was used to saturate the double bond. Molecular ions at *m/e* (418, 416, 414, 412), (338, 336, 334), (396, 394, 392), and (316, 314) were observed. Also, in the ^{1}H n.m.r. spectra of product mixtures formed under conditions in which excess of bromine was used we noticed a singlet at τ 5.5 which in successive experiments formed at the expense of the methyl signals at τ 7.65. We found that this signal (τ 5.5) became more significant in an experiment left for a longer reaction time and was absent or present in only trace measurement at lower concentrations. It would seem that aromatic substitution occurs after addition to the olefinic double bond, and does not compete appreciably with addition. We have however, no information as to whether the acetoxybromide adducts or dibromide adducts compete with olefin for bromine as would appear to be the case for



(3)
(erythro)



(4)
(threo)

*A previous paper [11] reads as if extraneous signals were detected with chlorine acetate due to a typographical error. No extraneous signals were detected.

[16] P. B. D. de la Mare and M. A. Wilson, *J.C.S. Perkin II*, 1973, 653.

[17] J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, 1903, **83**, 666; E. Berner and C. N. Riiber, *Ber.*, 1921, **54**, 1945.

[18] J. M. Agoff, M. C. Cabaleiro, and J. C. Podesta, *Chem. and Ind.*, 1974, 305.

chlorination by molecular chlorine and chlorine acetate for the *para*-methoxyolefin.[11] The products of addition of bromine acetate to phenylpropene were assigned by comparison of their ^{1}H n.m.r. spectra with the data recorded in the literature.[12]

The products of reaction of methyl *para*-methyl-*trans*-cinnamate were shown to be those of kinetic control by placing a mixture of *erythro*- and *threo*-dibromides in solution for the longer experimental times recorded for the experiments at lower concentration. A change in product ratio to that observed for the latter experiments did not occur. In view of this finding and with regards to the product ratios observed for the other olefins (with perhaps the exception of the *para*-methoxyolefin) it seems unlikely that isomerisation is occurring in these reactions as well.

DISCUSSION

Bromine acetate has been shown to initiate heterolytic electrophilic reactions in both polar [13,19] and non-polar [13,14,20] solvents and these results support the conclusions for acetic acid because the orientation of addition is shown to be the same as that of the corresponding additions initiated by molecular bromine. No products of anti-Markownikoff [21] addition were detected by ^{1}H n.m.r. spectroscopy for either electrophile on addition to the substrates investigated.

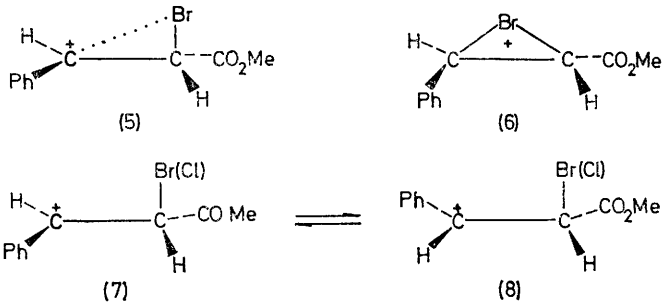
TABLE 4

Ratios of *anti* : *syn*-addition for the reaction [a] of bromine acetate (0.01M) and chlorine acetate [b] (0.01M) with some methyl *trans*-cinnamates ($R^3C_6H_4CH{=}CHCO_2Me$) (0.01M)

R^3	Electrophile	Ratio
p-OMe	ClOAc	5.3
p-OMe	BrOAc	>9.0
p-Me	ClOAc	1.6
p-Me	BrOAc	9.0
p-H	ClOAc	1.6
p-H	BrOAc	10
p-Cl	ClOAc	1.5
p-Cl	BrOAc	10
p-NO_2	ClOAc	3.3

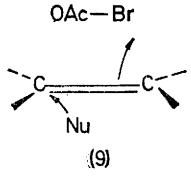
[a] Solvent is HOAc for ClOAc additions but 95% HOAc–5% CCl_4 for BrOAc additions. [b] Ref. 11.

In Table 4 are listed the ratios of *anti*- to *syn*-addition for these substrates, and the corresponding ratios with chlorine acetate. The results clearly indicate that bromine acetate is more stereospecific than chlorine acetate, as would be expected, since bromine is more capable of exerting stereochemical control over the reaction than chlorine. The more traditional explanation of this result would be to envisage bromonium ion formation (5) or (6) or both, followed by *anti*-attack to give the *erythro*-isomer (1; R^1 = Ac, R^2 = Me). A chlorine substituent would be less likely to bridge in this way by virtue of the fact that it is a poorer neighbouring group [22] and thus a contribution through (7) would be more likely. This may rotate to form (8). Addition to carbocation (7) from the side *anti* to bromine will give



rise to *erythro*-adduct (1; R^1 = Ac, R^2 = Me). However, addition to carbocation (8) from the side *anti* to bromine will produce *threo*-adduct (2; R^1 = Ac, R^2 = Me).

Alternatively (7) may give rise to *threo*-adduct (2; R^1 = Ac, R^2 = Me) and (8) may give *erythro*-adduct (1; R^1 = Ac, R^2 = Me) both by *syn*-addition. Another possibility, the Ad_E3 or $Ad3$ mechanisms [6,7,23] involving attack of solvent or other nucleophilic molecules (9)



remains a consideration but we have shown for chlorine acetate that in all except the *para*-nitro-case, that the substrates investigated give rise to similar or nearly similar ratio of products from both *cis*- and *trans*-olefins so it is likely that the equilibrium (7) ⇌ (8) is nearly established, if not completely so. However, the importance of an Ad_E3 pathway cannot be discounted at this stage for bromine acetate additions because of the large amount of *anti*-addition, although Olah has established bromonium ions as stable entities [24] and bromine is well known as a good neighbouring group.[7,22,25]

A comparison of product ratios from additions initiated by bromine and chlorine to the substrates investigated are shown in Table 5. The results show that in initiating additions to these substrates, bromine is more stereospecific than chlorine giving proportionally more *erythro*- than *threo*-dihalide and more *erythro*- than *threo*-acetoxyhalide.

The results with methyl *para*-methyl-*trans*-cinnamate (Table 3) indicate that with this compound appreciable overall *syn*-addition can occur in the intermediate range of concentration of bromine electrophile ([substrate] =

[19] P. B. D. de la Mare and J. L. Maxwell, *J. Chem. Soc.*, 1962, 4829.
[20] V. L. Heasley, C. L. Frye, G. E. Heasley, K. A. Martin, D. A. Redfield, and P. S. Wilday, *Tetrahedron Letters*, 1970, 1573.
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[22] S. Winstein, *Bull. Soc. chim. France*, 1951, C55.
[23] M. A. Wilson, *J. Chem. Educ.*, 1975, **52**, 495.
[24] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1967, **89**, 4744.
[25] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 1939, **61**, 1576, 2845.

2.5×10^{-2}—10^{-3}M, $[Br_2] = 2.5 \times 10^{-2}$—$2.5 \times 10^{-3}$M) and this is within the range of concentrations used in the additions to the other methyl *para*-substituted cinnamates.

It was first established by Robertson [27] and later confirmed for a wide variety of olefins of differing reactivity [8,9,28,29] that at the concentration $[Br_2] = 2.5 \times 10^{-2}$M the kinetic form of bromine additions is second order in bromine. Although the possible formation of Br_4 in pre-equilibrium cannot be eliminated, this requires the hypothesis that such a species is formed in sufficiently large concentrations to be kinetically significant.[4] The most probable explanation is that an initially formed complex (olefin, Br_2) is involved in the rate-determining stage and that the removal of bromide ion can be achieved either by solvent [9,30,31] or bromine.[8,9,30] Whether or not this complex is a molecular complex [32] (10), a three-centred bound alkenonium complex [33] (11), or involves considerable covalent bonding (12) or (13), or whether all may exist along the reaction co-ordinate is not clear. Support for the former comes from spectroscopic [34] and kinetic evidence [31,35] and for the latter from studies of substituent effects on aromatic substitution [36] where similar kinetic forms are obtained; and also from analogy with the preponderance of well known anionic species containing bivalent halogen.[37] It is probably significant to note that nuclear quadrupole resonance and Mössbauer spectroscopy have indicated that the charge is not located on the central atom [38] in these species, so the ion-pair like structure (14) may be a resonance contributor to this structure.[39]

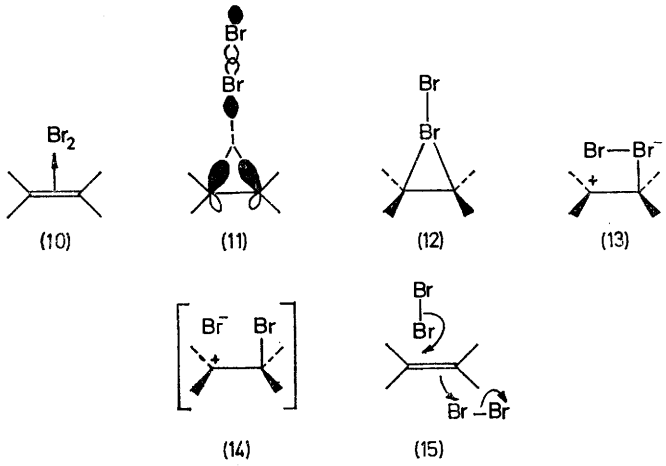
TABLE 5

Ratios of *anti-* : *syn*-addition for the reaction of bromine and chlorine [11,26] with some methyl *trans*-cinnamates ($R^3C_6H_4CH{=}CHCO_2Me$) (0.01M)

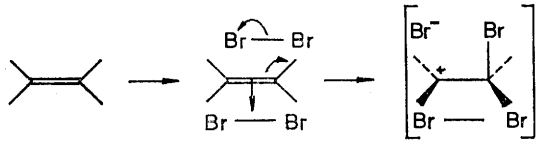
		Ratio	
R^3	Electrophile	Dihalides	Acetoxy-halides
p-OMe	Br_2 [a]	10.3	Large
p-OMe	Cl_2 [a]	2.3	
p-Me	Br_2 [a]	1.4	Large
p-Me	Cl_2 [a]	0.53	3.4
p-H	Br_2 [b]	6.8	Large
p-H	Cl_2 [b]	0.30	5.9
p-Cl	Br_2 [b]	5.9	Large
p-Cl	Cl_2 [b]	0.39	8.4
p-NO_2	Br_2 [b]	>20	
p-NO_2	Cl_2 [b]	Small	13.3

[a] [halogen] = 0.01M. [b] [halogen] = 0.1M.

An alternative mechanism has also been suggested. In this, the second molecule of bromine completes the addition in an Ad_E3 process (15). This mechanism has been thought unlikely [7] because similar kinetic terms are obtained in aromatic substitution. Here there would be no function for the second molecule of bromine.



Another possibility is that the first molecule of bromine might disrupt the double bond by co-ordination, but not actually provide nucleophile or electrophile in the addition step (16).

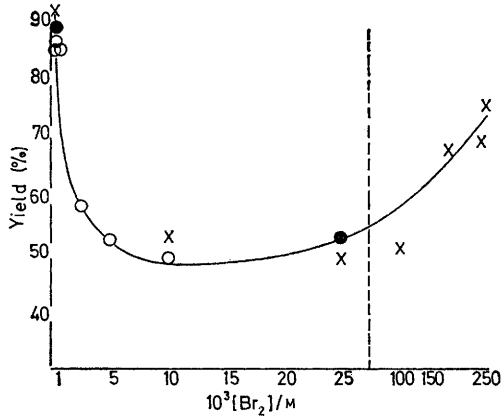


(16)

Our results have some bearing on these possibilities. We have found that unlike some other substrates reported in the literature [8,12] the amount of *syn*-addition to methyl *para*-methyl-*trans*-cinnamate is dependent on the concentration of electrophile (Figure). At lower concentrations (10^{-3}M) the reaction produces mostly *erythro*-dibromide. Only a little *threo*-dibromide and *erythro*-acetoxychloride are formed. This suggests that during additions to this substrate initiated by molecular bromine nucleophilic attack is occurring mostly on a

[26] M. C. Cabaleiro and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 565; M. D. Johnson and E. N. Trachtenberg, *ibid.*, 1968, 1018.
[27] P. W. Robertson, N. T. Clarke, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, 1937, 335.
[28] I. Ting and P. W. Robertson, *J. Chem. Soc.*, 1947, 628; H. P. Rothbaum, I. Ting, and P. W. Robertson, *ibid.*, 1948, 980.
[29] K. Yates and W. V. Wright, *Canad. J. Chem.*, 1967, **45**, 167; J. A. Pincock and K. Yates, *ibid.*, 1970, **48**, 2944.
[30] E. P. White and P. W. Robertson, *J. Chem. Soc.*, 1939, 1509.
[31] J. E. Dubois, F. Garnier, and R. H. Donnay, *Chem. Comm.*, 1971, 829.
[32] D. V. Banthorpe, *Chem. Rev.*, 1970, **70**, 295.
[33] G. A. Olah and T. R. Hockswender, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 3574.
[34] J. E. Dubois and F. Garnier, *Spectrochimica Acta*, 1967, **23A**, 2279.
[35] G. Salomon, *Discuss. Faraday Soc.*, 1947, **2**, 353; F. R. Mayo and J. J. Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339; C. G. Gebelein and G. D. Frederick, *J. Org. Chem.*, 1972, **37**, 2211.
[36] P. B. D. de la Mare in 'Theoretical Organic Chemistry,' Butterworths, London, 1958, p. 219; M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1957, 342; P. B. D. de la Mare and P. W. Robertson, *ibid.*, 1948, 100; P. B. D. de la Mare, *ibid.*, 1949, 2871.
[37] A. J. Downs and C. J. Adams in 'Comprehensive Inorganic Chemistry,' Pergamon, New York, 1973.
[38] C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, 1957, **27**, 1060; 1959, **30**, 1265; G. A. Bowmaker and S. Hacobain, *Austral. J. Chem.*, 1968, **21**, 551.
[39] P. B. D. de la Mare, C. J. O'Connor, and M. A. Wilson, *J.C.S. Perkin II*, 1975, 1150.

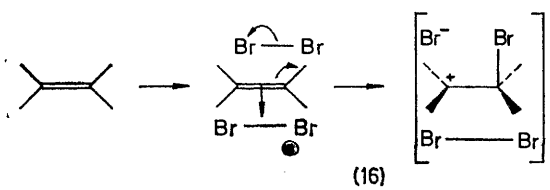
bridged species *e.g.* (5), (6), (11), (12), or (17) but that some *threo*-adduct arises by one of the pathways discussed previously. We also note that there is much less acetoxyhalide formation than with molecular chlorine. This is probably a reflection of the relative difference in nucleophilicity of Cl^-–OAc^-, HOAc, and Br_3^-–OAc^-, HOAc. The results with added sodium acetate support this; more acetoxybromide is formed, but only the *erythro*-isomer, and so it appears as if *syn*-attack is



Addition of bromine to methyl *p*-methyl-*trans*-cinnamate. Dependence of the yield of *erythro*-dibromide on the concentration of electrophile: ○, $[Br_2]$ = [olefin]; ×, $[Br_2]$ > [olefin] (see Table 3); ●, $[Br_2]$ = [olefin] (5% CCl_4 in solvent)

blocked by bridging, by a counter ion (14), or by the attached nucleophilic bromine atom in (13). At the concentration region studied in these experiments ($[Br_2]$ 10^{-3}M) the kinetic form of the reaction would be expected to be first order in bromine so the intermediates giving rise to products might be all or any of the species (5), (6), (11)—(13), and (17).

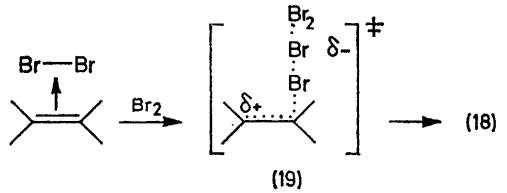
However, at high concentrations ($[Br_2] = 2.5 \times 10^{-2}$M) when the second order kinetic form in bromine is important, then if we accept that bromine removes bromide ion from complexed bromine, the high yield of *threo*-isomer observed makes a pathway through a bridged species unlikely to be the only route to *erythro*-adduct. At this concentration a species (18) must be



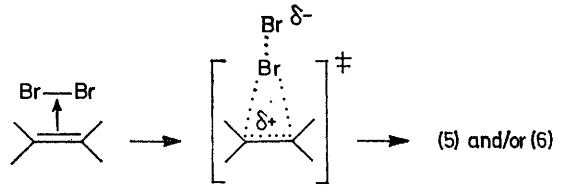
(16)

concerned which has bromide ion removed and which may collapse, *e.g.* after rotation and migration of Br_3^- to the reverse side, to give *threo*-adduct. Alternatively, a mechanism (16) in which the second molecule of bromine shields one side of the molecule may be occurring, but we dislike this possibility because added acetate gives diversion to *trans*-addition. If we choose the first consideration it means that the species involved in the process at low concentration must be different and more likely to bridge, or prevent rotation in some other way. For example (11)—(13) or (17) might be suggested. The addition reaction to give *erythro*-dibromide at low concentrations of bromine (10^{-3}M) could now be completed by molecular bromine or by the small amount of tribromide ion produced in the solution by acetoxybromide formation, but a further possibility is that bromide ion is now removed from species (11)—(13) or (17) by solvent to give (5) or (6) and that once the bridge is formed it does not open very often to form an open ion (7) ⇌ (8) because of the electron-withdrawing effect of the CO_2Me grouping. The bromide ion can now complete the addition by *anti*-attack.

An alternative which also seems reasonable is that at higher concentrations the bromine molecule removes bromide (19) from a molecular complex [8,9] to form an open ion but in the lower concentration region, the molecular complex reacts *via* a cyclic transition state (20) to form a bridged ion (5) or (6) which does not open very often to a non-bridged form before the product forming stage.



(19)



(20)

Yates and McDonald [40] suggest that cyclic transition non-bridged intermediates are formed further along states are involved in additions to stilbene, even if the reaction pathway. They found that initial enthalpy differences between *cis*- and *trans*-isomers are increased at the transition state. Their interpretation has been criticised however by Dubois [41] on the basis that the influence of substituents on the rate of bromination of some substituted stilbenes are best interpreted as a competition between three different pathways with transition states which are significantly different in their charge distributions. Our results may be interpreted as showing that different transition states may be available, for the same substrate, which are bridged or unbridged, depending on the reaction conditions.

Under the conditions investigated the stereochemistry observed for additions initiated by bromine acetate is not

[40] K. Yates and R. S. McDonald, *J. Org. Chem.*, 1973, **38**, 2465.
[41] J. E. Dubois and M. F. Ruasse, *J. Org. Chem.*, 1974, **39**, 2441; E. Bievenue-Goetz and J. E. Dubois, *ibid.*, 1975, **40**, 221.

dependent on concentration, so for additions initiated by molecular bromine whatever the interpretation given to the exact species involved before or after the transition state it seems reasonable to conclude that the bromine atom which does not become directly attached to the olefin (*i.e.* that part of molecular bromine which later becomes a potential nucleophile) has an important bearing on the stereochemistry of addition. This results when coupled with the fact that appreciable *syn*-addition of bromine can occur under conditions where second-order kinetics would be expected, suggests that for reactions of second order in bromine, attack of the second molecule of bromine occurs at the attached molecule of bromine, and that pathways such as (15) are unlikely in our systems at these concentrations.

At higher concentrations of bromine in other systems Swedlund and Robertson [42] detected kinetic terms of even higher order; and our results show that at higher concentrations of bromine (*ca.* 0.25M) more *erythro*-adduct is again formed. Very little mechanistic implications can be drawn for these concentrations at this stage, but the results are significant since *syn*- or *anti*-addition in many substrates in which carbonium ions are stabilised by electron-donating groups, may be dependent on a delicate balance of concentration.

The results for molecular bromine are directly comparable with those for bromine acetate, because although the solvent used for bromine acetate reactions contained 5% CCl_4, experiments with molecular bromine in acetic acid or 95% acetic acid–5% CCl_4 showed little variation in product ratios. We have shown that the ratios of acetoxychlorides formed with chlorine acetate are significantly different from those formed with molecular chlorine.[11] These results showed that different intermediates were involved with molecular chlorine than with chlorine acetate. However, because of the near stereospecific nature of the addition initiated by bromine acetate and the low yields of acetoxybromides formed in reactions initiated by molecular bromine we are unable to say if there are significant differences between acetoxybromide ratios formed by bromine acetate and molecular bromine. We hope to investigate this possibility with substrates which give appreciable *syn*-attack. We report some preliminary work on phenylpropene which indicates that acetoxybromides are readily formed in electrophilic additions initiated by bromine acetate to this substrate as well.

We conclude that our results show that the pathway by which bromine adds to olefinic substances is variable and so may be complex even for a given olefin. The picture is one of multiple intermediates which may give rise to different products depending on localised conditions.

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[5/653 *Received*, 7*th April*, 1975]

[42] B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 1947, 630.