Tetrahedron Letters No. 12, pp 1037 - 1040, 1975. Pergamon Press. Printed in Great Britain.

MECHANISMS OF ADDITION - 1:
The Addition of Bromine and Bromine Acetate to Some para-Substituted Cinnamates in Acetic Acid

by

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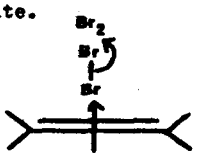
(Received in UK 27 January 1975; accepted for publication 12 February 1975)

Whereas the mechanism of bromination of olefinic substances by molecular bromine has been extensively investigated, the pathway by which bromine acetate (also called acetyl hypobromite) participates in addition has not been well explored.[1,2] In acetic acid at higher concentrations ($[Br_2]$ 2.5×10^{-2}M) bromine is believed to add by a pathway in which a first molecule of bromine is attached to the olefin,[1,3] and a second molecule removes halide from the attached bromine,[1,3,4] (1) or (2); i.e. the process does not proceed in the usual Ad_E3 sense.[2,5] The kinetics[6] and products[7] of addition of chlorine and chlorine acetate to some para-substituted cinnamates in acetic acid have recently been studied and this communication now extends these studies to bromine and bromine acetate. Product proportions are listed in Table 1 with the corresponding proportions with chlorine acetate.



(1)

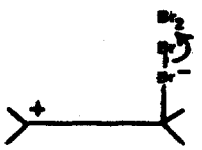


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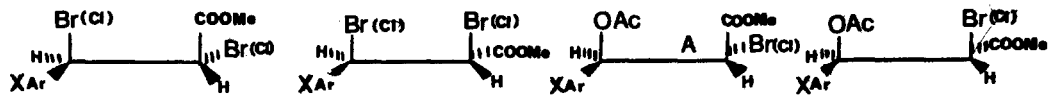
TABLE 1 PRODUCT PROPORTIONS FOR THE ADDITION OF VARIOUS ELECTROPHILES (E-Y) TO SOME PARA-SUBSTITUTED CINNAMATES IN ACETIC ACID (X-ArCH=CHCOOMe)

X	[E-Y]	E-Y	Product Proportions (3)	(4)	(5)	(6)
p-OMe[a]	10^{-2}M	BrOAc	-	-	100	-
p-OMe[a,b]	10^{-2}M	Br_2	72	7	21	-
p-Me	10^{-2}M	BrOAc	-	-	90	10
p-Me	10^{-2}M	Br_2	49	34	17	-
p-Me	2.5×10^{-2}M	Br_2	49	36	15	-
p-Me	1×10^{-1}M	Br_2	51	31	18	-
p-H	10^{-2}M	BrOAc	-	-	94	6
p-H[c]	10^{-2}M	Br_2	ca.75	-	ca.25	-
p-H	10^{-1}M	Br_2	58	11	28	3
p-Cl	10^{-2}M	BrOAc	-	-	90	10
p-Cl	10^{-1}M	Br_2	65	11	24	-
p-NO_2	10^{-1}M	Br_2	100	-	-	-
p-OMe[d]	10^{-2}M	ClOAc	-	-	84	16
p-Me[d]	10^{-2}M	ClOAc	-	-	61	39
p-H[d]	10^{-2}M	ClOAc	-	-	62	38
p-Cl[d]	10^{-2}M	ClOAc	-	-	60	40

a) for OMe there is evidence that aromatic substitution also occurs.

b) other products present c) Lit.Refn.8 d) Lit.Refn.7



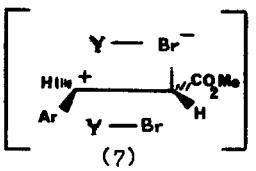
(3) (4) (5) (6)

(Formulations 3-6; only one enantiomer is shown but mixtures are racemic).

The results show that for these substrates bromine acetate adds regiospecifically just as chlorine acetate does. No products of anti-markownikoff[9] addition were detected by ^{1}H-n.m.r. spectroscopy for either electrophile, and it appears as others have shown[10] that bromine acetate is an electrophilic reagent in acetic acid. The results also show that bromine acetate is more stereospecific than chlorine acetate, as would be expected[11] because the bromine substituent is more capable of exerting stereochemical control over the reaction. For substrates which give appreciable amounts of threo-dichloride(4) and

threo-acetoxychloride(6) by overall syn-addition of chlorine and chlorine acetate, respectively, bromine acetate gives only a trace ($\leqslant$10%) of adduct from overall syn-addition. However, for methyl para-methyl-trans-cinnamate appreciable threo-dibromide(4) is formed with molecular bromine under the conditions shown, but for bromine acetate very little threo-acetoxybromide is formed. This is in marked contrast to the response of this substrate in reactions initiated by molecular chlorine and chlorine acetate. Where threo-dichloride represents an important part of the product produced in the reaction of molecular chlorine with the olefin, appreciable threo-acetoxychloride is formed in the reaction of the same substrate with chlorine acetate.

Several alternatives come to hand in explanation. One possibility is that for molecular bromine a pathway involving a route to threo-dibromide through (7; Y=Br) may be involved; but an analogous pathway (7; Y=OAc) is not available for bromine acetate. Alternatively, an ion pair (8) which can give rise to threo- and erythro-product is involved in molecular brominations but the ion (9) is not formed with bromine acetate because of proton transfer from the solvent. Instead, a free ion, which often bridges is formed. A third alternative is that an Ad_E3 process (10) or (11) makes an important contribution in reactions initiated by bromine acetate. We are currently investigating these possibilities by kinetic and product studies.



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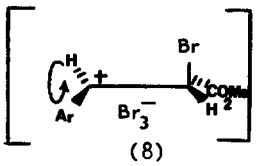

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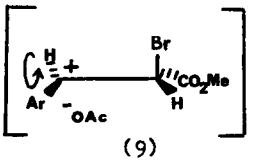

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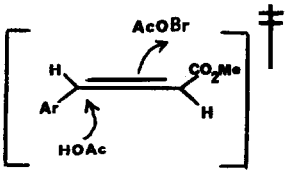

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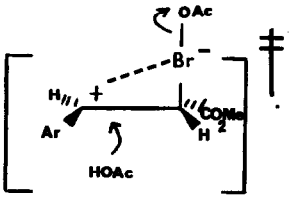

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