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EFFECT OF LITHIUM CHLORIDE ON THE BROMINATION OF METHYL CINNAMATES AND 1, 3-DIPHENYLPROPENONES.

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The influence of lithium chloride on the bromination of some α,β-unsaturated carbonyl compounds in acetic acid has been observed kinetically[1]. However, no information appears regarding the effect of the salt on the steric course of the reaction.

We have now examined the products and the stereochemistry of the addition of bromine to some representative α,β -unsaturated carbonyl compounds in acetic acid with and without added lithium chloride (Tables 1 and 2).

Examination of the kinetic behaviour of the series of esters shows that the reactions are initiated by electrophilic attack of bromine. The fact that the addition products from 4-Cl and 4-NO_2-cinnamates are exclusively those resulting from <u>trans</u>-addition suggests an intermediate which retains its stereochemical identity and this situation is consistent with reaction <u>via</u> a bridged bromonium ion. This type of intermediate must be more efficiently opened by attack of the bromide liberated on the first stage of the addition, which on nucleophillic grounds should be more active than the chloride[2].

On the other hand, addition to the more basic esters (4-R = CH_3, OCH_3) is much less stereoselective judging by examination of the products as was expected[3]. Thus, dibromides resulting from <u>trans</u> and <u>cis</u>-addition of bromine and adducts formed by diversion of the reaction to incorporation of the solvent and the added chloride ions are evidence in favour of an open bromonium intermediate, which reacts partially with the less nucleophilic chloride and acetate[2].

Comparison of the adduct composition from methyl <u>trans</u>-cinnamates (Table 1) and <u>trans</u>-1, 3-diphenylpropenones (Table 2) suggests that the predominant

TABLE 1

Proportions of adducts formed in reactions of bromine (0.0125 M) with methyl <u>trans</u>-cinnamates (0.0125 M) in acetic acid at 30°.

R	Added LiCl	$4\text{-}RC_6H_4CHX.CHBrCOOCH_3$					
		X = Br		OAc		Cl	
		Erythro	Threo	Erythro	Threo	Erythro	Threo
NO_2	-	100	-	-	-	-	-
	0.0125 M	100	-	-	-	-	-
	0.10 M	100	-	-	-	-	-
Cl	-	100	-	-	-	-	-
	0.0125 M	96	-	4	-	-	-
	0.10 M	96.5	-	3.5	-	-	-
H	-	97.5	-	2.5	-	-	-
	0.0125 M	96	-	2	2	-	-
	0.10 M	94	-	5	3	-	-
CH_3	-	44	29	20	7	-	-
	0.0125 M	57	22	13	8	-	-
	0.10 M	36	23	17	9	15	-
OCH_3	-	73	18	6	3	-	-
	0.0125 M	66	21	10	3	-	-
	0.10 M	61	27	4	4	4	-

mechanism in the bromination of the former in the presence of lithium chloride is different from that in the latter. This difference also arises from the kinetic results.

Thus, whereas the products of bromination of the series of esters are not altered or show little change by addition of lithium chloride the 1, 3-diphenylpropenones

TABLE 2

Proportions of adducts formed in the reactions of bromine (0.0125 M) with trans-1, 3-diphenylpropenones (0.0125 M) in acetic acid at 30°.

R	Added LiCl	$4\text{-}RC_6H_4CHX.CHBrCOC_6H_5$					
		X = Br		OAc		Cl	
		Erythro	Threo	Erythro	Threo	Erythro	Threo
NO_2	-	100	-	-	-	-	-
	0.0125 M	45	-	6	-	44	5
	0.10 M	14	-	-	-	85	11
Cl	-	95	5	-	-	-	-
	0.0125 M	42	-	4	-	45	9
	0.10 M	21	-	-	-	63	16
H	-	84	8	7	1	-	-
	0.0125 M	43	2	-	-	51	4
	0.10 M	11	-	4	2	76	7
CH_3	-	56	19	19	6	-	-
	0.0125 M	44	21	15	6	10	4
	0.10 M	31	23	17	2	18	9
OCH_3	-	60	29	9	2	-	-
	0.0125 M	61	15	10	7	6	1
	0.10 M	42	23	11	9	10	5

show a substantial response to the presence of the salt, and the reactions are associated with the formation of considerable amounts of bromochlorides.

On the other hand, whereas the rate of bromination of the esters with or without added lithium chloride is little affected by the presence of hydrogen chloride, the corresponding reactions with the ketones are strongly catalysed by the acid.

There is good evidence that the bromination of α,β-unsaturated ketones is catalysed by acids[1], involving an initial proton transfer reaction to form the conjugate base of the ketone followed by the nucleophilic attack of the halogen on the β-carbon atom. As acetic acid has been shown to protonate conjugated molecules[4], it seems likely from the present products analysis and kinetic results that the reaction of bromine with 1, 3-diphenylpropenones in the presence of lithium chloride proceeds partially through the formation of an intermediate resulting from the attack of the nucleophilic chloride on the protonated substrate, which would then be brominated in a subsequent step. Support for this view is found in the fact that the presence of sodium acetate in the medium of the reaction, which suppresses any acid catalysed nucleophilic addition[1], reduces markedly the yields of bromochlorides.

If the above assumption is correct substituents increasing the electron density on the β-carbon atom of the ketone would be expected to decrease the yield of bromochlorides by reducing the degree of nucleophilic attack, as is observed.

Products have been identified by ^1H n.m.r. spectroscopy and elimination reactions as described in earlier papers[5].

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