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HALOGENATION OF UNSATURATED ESTERS—III

REACTIONS OF BROMINE CHLORIDE WITH CHLORINATED METHYL 2-BUTENOATES

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Abstract—Additions of Cl_2, Br_2 and BrCl to methyl *Z*-2-chloro-2-(**1**), *E*-3-chloro-2-(**2**), *Z*-3-chloro-2-(**3**) and *E*-4-chloro-2-butenoates (**4**) in CCl_4 both in the dark and light have been investigated. The product compositions are compared with those reported previously for methyl monochloropropenoates. The chlorine substitution was found to affect the product distributions in the reactions with the BrCl reagent. Under the ionic conditions Br_2 adducts were the main products from **1** and **2**, whereas **3** reacted like methyl *Z*-3-chloropropenoate giving only negligible amount of the Br_2 addition. The Cl_2 addition amounted, as in the reactions of methyl monochloropropenoates, to only a few percent. Compared with the parent esters the chlorine substitutions in **2**, **3** and **4** also affected the regiochemistry of the BrCl addition. The main regioisomer in the dark, i.e. the 2-bromo-3-chloro adduct, was obtained from **3**, as from methyl *Z*-3-chloropropenoate, with almost complete regioselectivity. Compound **4** also showed greater regioselectivity than methyl *E*-2-butenoate. Substrate **2** was, however, found to produce more 3-bromo-2-chloro adduct than the unchlorinated parent ester. Mechanisms presented for the additions of BrCl to methyl 3-chloropropenoates are reconsidered on the basis of the results from the present study.

Bromine chloride adds to the C=C bond of α,β-unsaturated carbonyl compounds so that Br becomes attached, preferentially, to the α-position.[1–8] BrCl disproportionates in some organic solvents, e.g. in CCl_4,[9,10] but in spite of that the additions usually occur as if BrCl was the dominant reagent.[7,8,10–13] However, the reaction mixtures frequently also contain Br_2- and Cl_2-addition products.[2,7,8,11–16]

Previously we reported the reactions of methyl monochloropropenoates with Cl_2, Br_2 and BrCl.[8] The product distribution obtained with the BrCl reagent from methyl *Z*-3-chloropropenoate was found to differ markedly from those of methyl 2-chloro- and *E*-3-chloro isomers. The former gave in the dark only approx. 1% of the Br_2-addition products, whereas the latter gave these as the main products. Only negligible amounts ($\lesssim$ 1%) of Cl_2 additions were obtained. The different product distributions could not be attributed to differences in the reaction conditions. To study if the position of the Cl substituent influences the BrCl addition, the corresponding halogenation reactions were performed with methyl *Z*-2-chloro-2- (**1**), *E*-3-chloro-2- (**2**), *Z*-3-chloro-2- (**3**) and *E*-4-chloro-2-butenoates (**4**).

EXPERIMENTAL

Materials and methods

Compound **1** was synthesized from 2,3-dichlorobutanoic acid[17] via dehydrohalogenation[18] and esterification. Compounds **2** and **3** were prepared from the corresponding acids[19] via $SOCl_2$–MeOH treatment and **4** from 3,4-dichlorobutanoic acid[17] by HCl elimination[20] and esterification. The purity of compounds **1–4** was checked by GLC and the structure verifications were based on their NMR[21–23] and mass spectra (Table 1).

The halogenations of **1–4** were carried out simultaneously in dilute CCl_4 solns (to avoid radical reactions) using equiv amounts of halogen and substrate.[7,8] The BrCl reagent was prepared by conducting an equal amount of Cl_2 into Br_2 in an ice bath. The mixture was irradiated by UV light for 3 hr and left to stand in the cold overnight before use. The halogenations were performed at room temp in the dark, and at about −20° in light. The reactions were followed by GLC and allowed to proceed to completion.

The dehydrohalogenations for the addition products of **2–4**, i.e. 2,3,3- and 2,3,4-trihalo isomers, were performed as described earlier.[5,7,8] The 2,3- and 2,4-dihalo-2-butenoates formed were identified by GLC and GLC–MS. The former were compared with authentic samples, obtained by the halogenation of methyl 2-butynoate.[24,25]

A Perkin–Elmer Sigma 3 gas chromatograph equipped with a FID-detector, an OV-101 quartz capillary column (25 m × 0.30 mm ID) and a Hewlett–Packard Model 3390A Reporting Integrator were used for the GLC analyses. The N_2-carrier gas flow rate was 1 ml/min. GLC–MS studies were performed with a Varian MAT-212 mass spectrometer, connected to a Varian Model 3700 gas chromatograph (OV-101 column). The GLC–MS data were acquired and processed on a Spectro-System MAT-188. The five most abundant MS peaks of each compound are given in Table 1; ions containing ^{37}Cl or ^{81}Br are not shown. The NMR spectra were obtained with a Perkin–Elmer R 12 B or a JEOL FX 60 spectrometer.

RESULTS AND DISCUSSION

Identification of the addition products

The addition products were not all separated individually but were identified from the product mixtures by ^{1}H-NMR, GLC and GLC–MS. The separation of the diastereomers of the regioisomeric and Cl_2- and Br_2-addition products was accomplished by GLC except in the case of **1**.

The structural information given by the elimination products was made use of as described earlier.[5,7,8] The configurations of the diastereomeric compounds could not, however, be determined unambiguously on the basis of the dehydrohalogenation products. The diastereomeric compounds are denoted in Table 1 by the same compound number and an accompanying letter referring to their mutual GLC eluting order.

The starting materials are eluted on OV-101 in the

Table 1. GLC–MS data for chlorinated methyl 2-butenoates (1–4) and their halogenation products (5–16)

No.	Compound	Mass spectrum,[a] *m/z* (%, rel. int.)	GLC retention time (min)[b]
1	Methyl *Z*-2-chloro-2-butenoate	134 (79, M), 103 (100), 102 (49), 75 (81), 39 (83)	6.39
2	Methyl *E*-3-chloro-2-butenoate	134 (32, M), 103 (100), 99 (59), 59 (16), 39 (32)	5.27
3	Methyl *Z*-3-chloro-2-butenoate	134 (22, M), 103 (100), 99 (38), 75 (18), 39 (53)	6.54
4	Methyl *E*-4-chloro-2-butenoate	134 (19, M), 103 (100), 102 (28), 75 (42), 39 (67)	7.54
5	Methyl 2,2,3-trichlorobutanoate	204 (—, M), 142 (28), 110 (100), 75 (48), 59 (57), 39 (35)	10.67
6	Methyl 2-bromo-2,3-dichlorobutanoate	248 (—, M), 154 (61), 103 (49), 75 (86), 59 (87), 39 (100)	12.75
7	Methyl 3-bromo-2,2-dichlorobutanoate	248 (—, M), 110 (100), 103 (15), 75 (61), 59 (72), 39 (48)	12.58
8	Methyl 2-chloro-2,3-dibromobutanoate	292 (—, M), 134 (33), 103 (49), 75 (78), 59 (79), 39 (100)	14.68
9	Methyl 2,3,3-trichlorobutanoate	204 (—, M), 110 (80), 108 (100), 75 (38), 59 (77), 39 (53)	9.85
10	Methyl 2-bromo-3,3-dichlorobutanoate	248 (—, M), 103 (53), 99 (33), 75 (44), 59 (86), 39 (100)	12.00
11a	Methyl 3-bromo-2,3-dichlorobutanoate	248 (—, M), 169 (20), 103 (16), 75 (57), 59 (100), 39 (53)	12.06
11b	Methyl 3-bromo-2,3-dichlorobutanoate	248 (—, M), 169 (20), 103 (17), 75 (61), 59 (100), 39 (58)	12.19
12a	Methyl 3-chloro-2,3-dibromobutanoate	292 (—, M), 213 (28), 103 (46), 75 (37), 59 (99), 39 (100)	13.97
12b	Methyl 3-chloro-2,3-dibromobutanoate	292 (—, M), 103 (40), 99 (22), 75 (36), 59 (95), 39 (100)	14.12
13a	Methyl 2,3,4-trichlorobutanoate	204 (—, M), 110 (63), 83 (33), 75 (87), 59 (100), 39 (36)	13.09
13b	Methyl 2,3,4-trichlorobutanoate	204 (—, M), 133 (34), 110 (47), 75 (69), 59 (100), 39 (31)	13.32
14a	Methyl 2-bromo-3,4-dichlorobutanoate	248 (—, M), 134 (38), 103 (61), 75 (82), 59 (75), 39 (100)	14.82
15a	Methyl 3-bromo-2,4-dichlorobutanoate	248 (—, M), 133 (45), 103 (37), 75 (94), 59 (100), 39 (64)	14.58
15b	Methyl 3-bromo-2,4-dichlorobutanoate	248 (—, M), 133 (58), 105 (23), 75 (91), 59 (100), 39 (49)	14.63
16a	Methyl 4-chloro-2,3-dibromobutanoate	292 (—, M), 133 (65), 103 (68), 75 (58), 59 (77), 39 (100)	16.21
16b	Methyl 4-chloro-2,3-dibromobutanoate	292 (—, M), 133 (61), 103 (69), 75 (61), 59 (82), 39 (100)	16.44

[a] Five most abundant peaks, ions containing ^{37}Cl or ^{81}Br are not shown.
[b] For operating conditions see Experimental.

order: *E*-3-chloro (**2**) < *Z*-2-chloro (**1**) < *Z*-3-chloro (**3**) < *E*-4-chloro (**4**) ester. The retention times of the trihalo products increase with increasing molecular weight, as expected.[7,8]

The MS molecular ion peaks are not shown in the mass spectra of the trihalo products (Table 1). The ions formed by α-cleavages, accompanied by the loss of one or two halogen atoms, are characteristic. The 2-halo isomers can, in general, be distinguished based on a McLafferty rearrangement ion, i.e. 2-chloro, 2,2-dichloro, 2-bromo and 2-bromo-2-chloro isomers having peaks at *m/z* 108, 142, 152 and 186, respectively. This fragmentation gives the base peak in methyl 2,3,3-trichlorobutanoate (**9**). The bromo isomers show weaker McLafferty peaks, but display relatively more abundant primary loss of a halogen atom. The bromine and chlorine are preferentially lost from the 2- and 3-positions, respectively, and a geminal different halogen atom seems to prevent these losses.

Compounds **6** and **7** can be differentiated based on the $(CH_3—CH=CX_2)^{+\cdot}$ fragment ion. This fragmentation gives the peak at *m/z* 110 in **7** and at *m/z* 154 in **6**. Compound **10**, bearing one Br atom at position 2 and two Cl atoms at position 3, can be expected to give more easily than **11** the fragment ion with *m/z* 103, formed by the loss of two halogen atoms accompanied by the α-cleavage. This is evident from Table 1, which shows that this fragmentation gives the base peak (*m/z* 103) in the unsaturated 3-chloro esters (**2** and **3**). The same trend is observed in the compound pair **13** and **14**.

Additions of chlorine and bromine

The relative reactivities of the halogens towards the starting esters were found to be $Cl_2 < BrCl \lesssim Br_2$. The reactivity order of **1**–**4** towards Cl_2 and Br_2 in CCl_4 was **1** > **3** > **2** > **4** and **3** > **2** > **1** > **4**, respectively, the differences however being slight.

Stereoisomers, i.e. enantiomers (a racemic mixture) and/or diastereomers were formed in all the reactions studied. Table 2 gives the diastereomer ratios of the bromine addition products. The corresponding data for methyl monochloropropenoates are included for comparison.[8]

Chlorination leads to the formation of diastereomers only in the case of methyl *E*-4-chloro-2-butenoate (**4**). The diastereomer ratio was 81 : 19 (in the dark). The bromination of methyl *Z*-2-chloro-2-butenoate (**1**) should also give diastereomers. However, only one GLC peak was observed both in the dark and light. This does not indicate complete stereoselectivity because it is possible that the diastereomers were not separated on the column used.

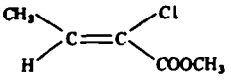
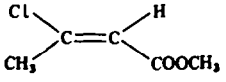
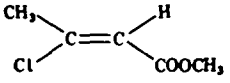
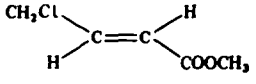
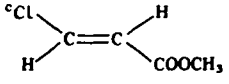
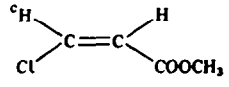
Some isomerization (**2** → **3**) was found to occur during the bromination of methyl *E*-3-chloro-2-butenoate (**2**). Analogous isomerizations have been reported earlier.[8,25,26]

Additions of bromine chloride

The regioisomer and diastereomer ratios and the relative proportions of the various products of the BrCl additions are presented in Table 3. The corresponding data for methyl monochloropropenoates are included for comparison.[8]

The 2-bromo-3-chloro adducts were the main regioisomers in the dark and the 3-bromo-2-chloro adducts in light, except for substrate **1**, which gave the regioisomers in about the same ratio (72 : 28, 77 : 23) under both reaction conditions. This may be a sign of a primarily ionic mechanism also in light, as has been reported for methyl *E*-2-butenoate (70–75 : 30–25).[5,7] The 2-bromo-3-chloro addition to **1** should give a pair of diastereomers, but evidently these were not separated on GLC just as in the case of the Br_2 addition. Thus, the stereoselectivity of this reaction remained

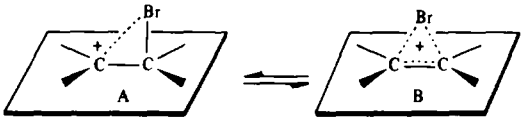
Table 2. Diastereomer distributions in the brominations of compounds 1–4

Substrate		Diastereomer ratio (a : b)[a]	
		Dark reaction	Light reaction
	(1)	[b]	[b]
	(2)	76:24	87:13
	(3)	3:97	24:76
	(4)	98:2	91:9
		62:38	96:4
		32:68	92:8

[a] Notation a : b refers to the GLC retention order of the diastereomers.
[b] Only one GLC peak was observed, see Discussion.
[c] From Ref. 8.

uncertain. The ratios of the diastereomers formed in the 3-bromo-2-chloro additions to **2** and **3** are shown in Table 3.

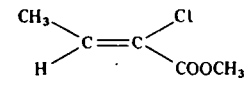
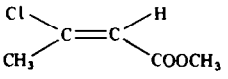
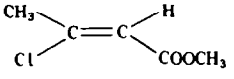
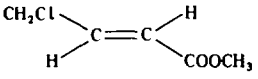
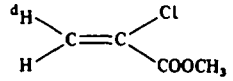
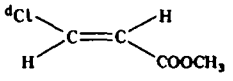
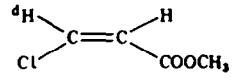
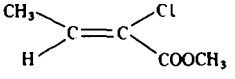
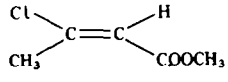
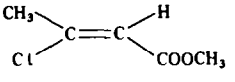
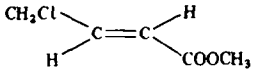
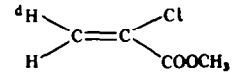
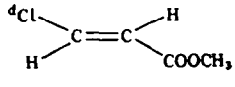
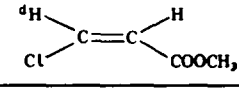
The almost complete regioselectivity of the reactions of **3** and **4** (in the dark) refers to a strongly unsymmetrical intermediate, represented simply by A. In the case of substrates **1** and **2**, the charge is more evenly dispersed as in B. The regioisomer ratio for **2** (71 : 29) indicates less regioselective addition than reported for methyl *Z*-2-butenoate (93 : 7).[5]



In the previous paper dealing with methyl *E*- and *Z*-3-chloropropenoates we assumed, without proving the configurations of the diastereomers, that the addition of Br_2 in the dark occurs predominately in the *anti*-sense.[8] To prove this we have tried to solve the configurations by ^{1}H-NMR. A vicinal coupling constant of 10 Hz was found for methyl 3-chloro-2,3-dibromopropanoate, obtained in light with a diastereomer ratio of 96 : 4 (Table 2) from methyl *E*-3-chloropropenoate. This refers to the *anti*-orientation of H-2 and H-3, but does not, however, aid in the identification, since the most stable rotational form for both the 'erythro' and 'threo' isomer is evidently one with *anti*-orientation of H-2 and H-3 relative to each other.

It was also reported that in the 3-bromo-2-chloro addition (to methyl *E*- and *Z*-3-chloropropenoates) the *syn* products were predominately formed.[8] This was based on the HX elimination, the low stereospecificity of the Br_2 addition and the known appearance of *syn*-addition products in aprotic solvents. In the dark methyl *E*-3-chloropropenoate gave the 3-bromo-2,3-dichloro product with a diastereomer ratio 94 : 6 and this product gave with triethylamine methyl *Z*-2,3-dichloropropenoate (possible to form by *anti* elimination only from the *syn*-addition product). The experience of the HX elimination from the present study however makes this argument questionable; the elimination does not seem to be as simple as was supposed, i.e. the product is evidently not always formed with the retention of the geometry. In view of the product distributions it seems that methyl 3-chloropropenoates and 3-chloro-2-butenoates react with BrCl by analogous mechanisms and thus, that in the dark the 3-bromo-2-chloro products are primarily formed by *anti* addition also from the former.

Table 3. Product distributions in the reactions of compounds 1–4 with bromine chloride

Substrate		Relative product proportions in the reactions with BrCl				
		Cl_2-addn. product	Br_2-addn. product	BrCl-addn. product	Regioisomer ratio 2-Br-3-Cl : 3-Br-2-Cl	Diastereomer ratio (a : b)[a] of 3-Br-2-Cl regioisomer
Additions in the dark						
	(1)	2	69	29	72:28[b]	
	(2)	2	54	44	71:29	65:35
	(3)	9	3	88	98:2	~0:100
	(4)	Trace	33	67	94:6[c]	
		0	64	36	40–47:53–60	
		1	53	47	88:12	94:6
		0	1	99	98:2	45:55
Additions in light						
	(1)	9	33	58	77:23[b]	
	(2)	4	55	41	17:83	70:30
	(3)	4	54	42	37:63	66:34
	(4)	2	79	19	5:95[e]	94:6
		—	—	—	45:55	
		3	40	57	31:69	82:18
		3	40	57	47:53	83:17

[a] Notation a : b refers to the GLC retention order of the diastereomers.

[b] Only one GLC peak represented methyl 2-bromo-2,3-dichlorobutanoate.

[c] The diastereomer ratio a : b of methyl 2-bromo-3,4-dichlorobutanoate was 97 : 3. The diastereomer ratio of methyl 3-bromo-2,4-dichlorobutanoate remained undetermined due to the small relative proportion (4%) of this regioisomer and partial overlapping of the GLC peaks.

[d] From Ref. 8.

[e] The diastereomer ratio of methyl 2-bromo-3,4-dichlorobutanoate remained undetermined for the reasons given in footnote c.

Formation of the Br_2-addition products with the BrCl *reagent*

As shown in Table 3 the reactions with the BrCl reagent produced under both reaction conditions substantial amounts of the Br_2-addition products, except for substrate **3** (approx. 3%) in the dark. The corresponding percentages from **1**, **2** and **4** vary between 33–69%. However, the Cl_2 addition amounted to only 9% at most (Table 3). Thus the disproportionation of BrCl cannot alone explain the product distributions.[9,14,15] Also the formation of the Br_2 products by halogen exchange after addition can be excluded, because the reactions were followed by GLC and the relative product proportions were found to remain the same. The diastereomer ratios of the Br_2 products obtained with the BrCl reagent differed only slightly or not at all from those of the corresponding products obtained with Br_2.

All reactions of **1**–**4** were slow in the dark (about 5 days to completion). The reactivities towards the BrCl reagent differed slightly: *Z*-2-chloro (**1**) > *E*-3-chloro (**2**) > *E*-4-chloro (**4**) > *Z*-3-chloro (**3**). The relative proportions of the Br_2 products in the reaction mixtures were 69, 54, 33 and 3%, respectively. As previously shown the reactivity order of methyl monochloropropenoates towards the BrCl reagent was 2-chloro $\gtrsim$ *E*-3-chloro > *Z*-3-chloro and the relative proportions of the Br_2 products were 64, 53 and 1%, respectively (Table 3).[8] Substrates **3**, **4** and methyl *Z*-3-chloropropenoate, which showed almost complete regioselectivity with BrCl, gave least Br_2 adducts and substrates **1**, **2** and methyl 2-chloro- and *E*-3-chloropropenoates which, according to the regioisomer ratios, reacted through less polarized intermediates, gave most Br_2 adducts. Thus, this might suggest that the strongly (A) and weakly (B) polarized intermediates differ in reactivities towards the nucleophiles present.[27–30]

Additions of Cl_2 and Br_2 to α,β-unsaturated carbonyl compounds are subject to catalysis by acid, particularly, by hydrogen halide.[6,29,30,31] These reactions tend to be autocatalytic and even trace amounts of HX may be effective. In light the halogenations of **1**–**4** were slow in the beginning, but the rates increased rapidly with a strong evolution of hydrogen halide, evidently formed by substitution reactions. The influence of the HX catalysis on the product distributions was not investigated. In the dark the formation of HX was not shown.

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