Tetrahedron Vol. 38, No. 18, pp. 2837 to 2841, 1982
Printed in Great Britain.

0040-4020/82/182837-05$03.00/0
Pergamon Press Ltd.

ADDITION OF CHLORINE, BROMINE AND BROMINE CHLORIDE TO SOME α, β-UNSATURATED METHYL ESTERS

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(*Received in the UK 4 February* 1982)

Abstract—The additions of chlorine, bromine and bromine chloride to *trans* methyl 2-butenoate **1**, *trans* methyl 2-methyl-2-butenoate **2** and methyl 3-methyl-2-butenoate **3** under ionic conditions were studied. Bromine chloride addition always gave as a major regioisomer the 2-bromo-3-chloro compound, almost quantitatively in the case of **3**. The mechanism of bromonium ion ring-opening (S_N1 or S_N2) is discussed with respect to the double bond substitution and regioisomer proportions. The dihalo products were identified by MS, ^1H and ^{13}C NMR.

As a continuation to our investigations concerning chlorinated esters,[1,2] we decided to study the reactions of chlorine, bromine and bromine chloride towards three different α, β-unsaturated ester double bonds.

Heasley *et al.*[3] have reported the addition of bromine chloride to methyl acrylate, methyl isocrotonate and methyl crotonate under ionic and radical conditions in methylene chloride. Under ionic conditions, the prevailing isomer was in all cases the 2-bromo-3-chloro compound. According to them, methyl crotonate gave most (30%) and methyl isocrotonate least (7%) 3-bromo-2-chloro isomer, analysed as the elimination products. Hydrogen halide elimination with triethylamine was initiated exclusively by attack of the base on the acidic α-hydrogen.[4] Because the bromochlorides could not be separated, even by glass capillary GC, we also used this elimination procedure for the analyses of 2-bromo/2-chloro regioisomer relations, which are considered with respect to the possible reaction mechanisms.

Reactivity of halogen towards the double bond varied from substrate to another. Differences were also evident between the reactivities of halogens towards the given substrate. Especially one of the products (methyl 2,3-dichloro-3-methylbutanoate), turned out to be relatively unstable giving rise to unsaturated monochloro compounds.

EXPERIMENTAL

Materials. Trans methyl 2-butenoate **1**, *trans* methyl 2-methyl-2-butenoate **2** and methyl 3-methyl-2-butenoate **3** were prepared *via* thionyl chloride and methanol treatment from commercial crotonic (Fluka, AG), tiglic (Merck) and senecioic acids (Merck). Equimolar amounts of halogens were added to about 10% CCl_4 solutions of the esters. Chlorine and bromine chloride (from equimolar amounts of Br_2 and Cl_2) were added as CCl_4 solutions whereas bromine was added neat. The halogenations were carried out at 0°, **3** being chlorinated also at −50 and −70°. The reactions were allowed to proceed for two days whereafter the solvent was evaporated and the reaction mixtures investigated by GC and further fractionated by vacuum distillation. At the end of the chlorinations the amounts of the substrates were about 10% except in the case of **3**. The other halogenations, however, occurred more completely.

The progress of the dehydrohalogenations[4] with triethylamine (Fluka, AG) was followed by GC and the reactions allowed to proceed for three days or until elimination had either occurred completely, or no further change could be noticed.

GC analyses were run by using a Varian Model 2400 gas chromatograph, with a flame-ionization detector and a 50 m × 0.3 mm (i.d.) 3% Carbowax 20M glass capillary column. The following running conditions were used: the column temperature programmed from 50° at 4°/min, carrier gas (N_2) flow-rate 1 ml/min, the splitting ratio 1:20 and the temperatures of injector and detector 230 and 250°, respectively.

Mass spectra were recorded on a Varian MAT-212 mass spectrometer, with a Varian Model 3700 gas chromatograph. A 5% SE-54 glass capillary column (25 m × 0.3 mm i.d.) with a flow-rate of helium of 1 ml/min was used. Electron energy was 70 eV and ion source temperature 220°. Data were acquired and processed on a Spectro System MAT-188.

^{13}C NMR spectra were obtained on a JEOL FX-60 Spectrometer as described earlier.[5] The sample concentrations varied between about 3–10% (w/w) in CCl_4 according to ^1H NMR. TMS served as an internal reference. The standard measurement error is 0.1 ppm for the chemical shifts. J(CH) coupling constants from the coupled spectra were used in the assignment of carbon resonances.

^1H NMR spectra were run with a 60 MHz Perkin–Elmer R 12 B Spectrometer. The shifts were measured with respect to locked TMS signal.

RESULTS AND DISCUSSION

Halogenation of trans *methyl 2-butenoate* **1**, trans *methyl 2-methyl-2-butenoate* **2** *and methyl 3-methyl-2-butenoate* **3**

The methyl dihalobutanoates formed in the nine processes were as follows: methyl 2,3-dichloro- **4**, 2-bromo-3-chloro- **5a**, 3-bromo-2-chloro- **5b**, 2,3-dibromo- **6**, 2,3-dichloro-2-methyl- **7**, 2-bromo-3-chloro-2-methyl- **8a**, 3-bromo-2-chloro-2-methyl- **8b**, 2,3-dibromo-2-methyl- **9**, 2,3-dichloro-3-methyl- **10**, 2-bromo-3-chloro-3-methyl- **11a**, 3-bromo-2-chloro-3-methyl- **11b** and 2,3-dibromo-3-methylbutanoate **12**. Gas chromatographic separation of a mixture of compounds **1–12** is illustrated in Fig. 1.

Compounds **4–9** are assumed to be the erythro forms as a result of the *trans*-additions. The retention time of **4** was compared with that of authentic erythro methyl 2,3-dichlorobutanoate.[2] The amounts of the threo forms were at the most a few per cent, confirmed as the diastereomers by GC/MS, their retention times being always longer than those of the erythro forms.[2]

Methyl 2-methyl-2-butenoate **2** and methyl 3-methyl-2-butenoate **3** reacted almost more violently with chlorine than methyl 2-butenoate **1**. Compared to the other 2,3-dichloro products, **10** is destable and eliminate spontaneously HCl. The relative proportion of **10** increased only slightly with decrease in the chlorination temperature. The main product in the chlorination mixture is an unsaturated monochloro ester, evidently methyl 2-chloro-3-methyl-3-butenoate (^1H NMR and GC/MS),

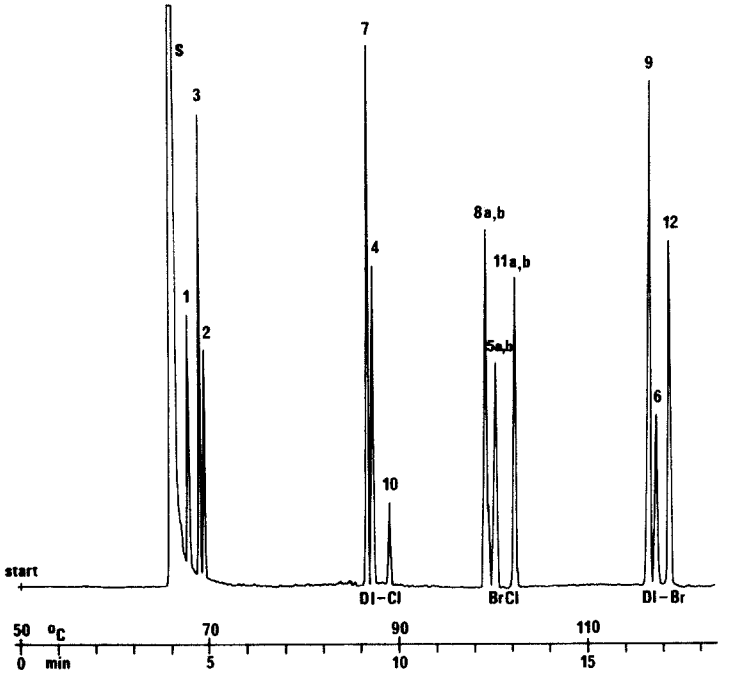

Fig. 1. Gas chromatogram of a mixture of methyl butenoates and their major halogenation products, separated on Carbowax 20 M glass capillary column. S = solvent; peaks identified in the text. For operating and other details see the Experimental section.

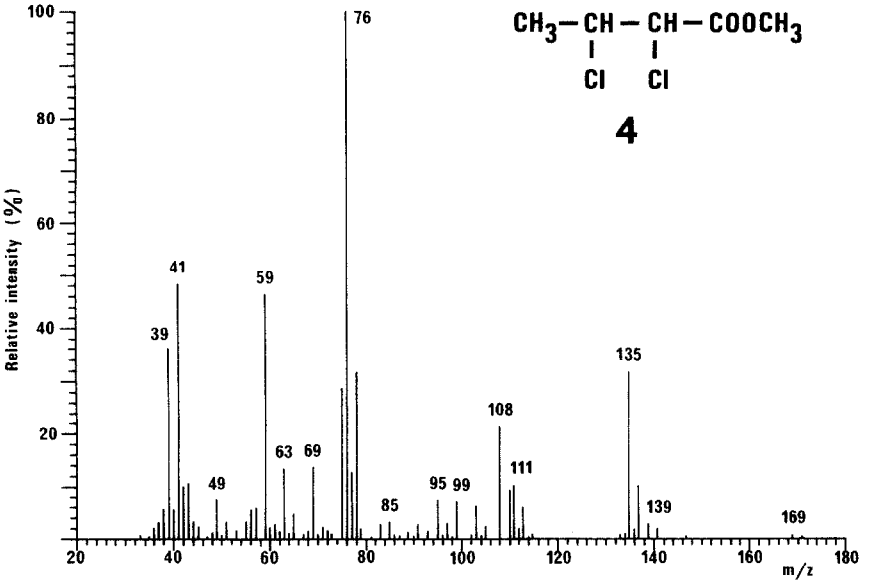

Fig. 2. 70 eV mass spectrum of erythro methyl 2,3-dichlorobutanoate **4**.

which presumably adds chlorine easier than **3** explaining the quite high amount of the unreacted substrate in the reaction mixture.

The bromine and bromine chloride additions were more vigorous with all substrates than were the chlorinations. The reactions with bromine chloride produced a few per cent of the dichloro and dibromo compounds according to GC analyses. Unsaturated monohaloesters could also be identified (GC/MS) from most reaction mixtures.

The bromine chloride additions gave regioisomer pairs **5a**, **5b**; **8a**, **8b** and **11a**, **11b**. The hydrogen halide eliminations with triethylamine led to the 2-halo-2,3-unsaturated esters, identified by GC through comparison with authentic samples. The ratios **5a**:**5b** and **11a**:**11b** were 75:25 and 96:4, respectively. However, about 10% of the mixture **5a**, **5b** and most of **11a**, **11b** remained unreacted in the base treatment. The easier elimination of HBr from **5a**, **5b** could be stated based on GC analyses. Taking into consideration this and the fact that the bromo compounds have obviously the greater weight response factors owing to their longer elution times (Fig. 1) the relative proportions of **5a** and **11a** are still greater than those given above. Owing to the absence of the acidic

Table 1. The characteristic fragment ions of the major halogenation products of methyl butenoates.

Fragment ion	Methyl butanoate, m/z (rel. int. %)								
	4	**7**	**10**	**5a,5b**	**8a,8b**	**11a,11b**	**6**	**9**	**12**
$\|M-OCH_3\|^+$	139 (3)	153 (1)	153 (2)	183 (2)	197 (-)	197 (2)	227 (-)	241 (-)	241 (-)
$\|M-COOCH_3\|^+$	111 (10)	125 (11)	125 (11)	155 (5)	169 (2)	169 (5)	199 (2)	213 (1)	213 (-)
$\|CRX-C(OH)OCH_3\|^{+\cdot}$	108 (21)	122 (31)	108(100)	108 (2) 152 (2)	122 (1) 166 (1)	108 (1) 152 (48)	152 (-)	166 (-)	152 (1)
$\|CRX-COOCH_3\|^+$	107 (1)	121 (3)	107 (-)	107 (2) 151 (-)	121 (2) 165 (-)	107 (1) 151 (-)	151 (?)[a]	165 (4)	151 (1)
$\|CH_3-CRX\|^+$	63 (14)	63 (13)	77 (64)	63 (5) 107 (2)	63 (3) 107 (1)	77 (38) 121 (4)	107 (2)	107 (1)	121 (2)
$\|CRX(OCH_3)\|^+$	79 (2)	93 (8)	79 (-)	79 (-) 123 (2)	93 (17) 137 (1)	79 (13) 123 (1)	123 (1)	137 (5)	123 (1)
$\|M-X\|^+$	135 (31)	149 (11)	149 (19)	179 (6) 135 (52)	193 (-) 149 (13)	193 (5) 149 (40)	179 (36)	193 (11)	193 (10)
$\|M-X-CO\|^+$	107 (1)	121 (3)	121 (2)	151 (-) 107 (1)	165 (-) 121 (2)	165 (2) 121 (4)	151 (17)[a]	165 (4)	165 (4)
$\|M-X-CH_3OH\|^+$ $\|M-HX-OCH_3\|^+$	103 (6)	117 (1)	117 (3)	147 (-) 103 (9)	161 (-) 117 (2)	161 (2) 117 (2)	147 (4)	161 (1)	161 (1)
$\|M-X-COOCH_3\|^{+\cdot}$	76(100)	90(100)	90 (20)	120 (23) 76 (13)	134 (7) 90 (8)	134 (5) 90 (2)	120 (4)	134 (2)	134 (-)
$\|M-X-CO-CH_3OH\|^+$ $\|M-HX-COOCH_3\|^+$	75 (29)	89 (20)	89 (20)	119 (5) 75 (27)	133 (1) 89 (8)	133 (4) 89 (13)	119 (10)	133 (3)	133 (4)
$\|M-X-HX\|^+$	99 (7)	113 (13)	113 (27)	99 (23)	113 (10)	113 (66)	99 (19)	113 (14)	113 (24)
$\|M-X-X\|^{+\cdot}$	100 (-)	114 (8)	114 (6)	100 (8)	114 (13)	114 (26)	100 (11)	114 (23)	114 (21)
$\|M-X-X-CH_3\|^+$	85 (3)	99 (4)	99 (2)	85 (23)	99 (9)	99 (6)	85 (20)	99 (15)	99 (7)
$\|M-X-X-OCH_3\|^+$	69 (14)	83 (11)	83 (29)	69 (83)	83 (27)	83 (90)	69 (89)	83 (34)	83 (84)
$\|M-X-X-CH_3OH\|^{+\cdot}$	68 (1)	82 (3)	82 (6)	68 (8)	82 (9)	82 (17)	68 (7)	82 (13)	82 (14)
$\|M-X-X-COOCH_3\|^+$	41 (48)	55 (62)	55 (61)	41(100)	55(100)	55(100)	41(100)	55(100)	55(100)
$\|COOCH_3\|^+$	59 (47)	59 (16)	59 (54)	59 (65)	59 (30)	59 (47)	59 (63)	59 (24)	59 (35)
$\|C_4H_5\|^+$	53 (1)	53 (30)	53 (51)	53 (2)	53 (27)	53 (50)	53 (3)	53 (20)	53 (34)
$\|C_3H_7\|^+;\|C_2H_3O\|^+$	43 (11)	43 (2)	43 (23)	43 (9)	43 (32)	43 (26)	43 (10)	43 (5)	43 (22)
$\|C_3H_6\|^{+\cdot};\|C_2H_2O\|^{+\cdot}$	42 (10)	42 (1)	42 (14)	42 (6)	42 (7)	42 (11)	42 (9)	42 (2)	42 (6)
$\|C_3H_5\|^+$	41 (48)	41 (2)	41 (57)	41(100)	41 (18)	41 (40)	41(100)	41 (5)	41 (23)
$\|C_3H_3\|^+$	39 (36)	39 (11)	39 (45)	39 (73)	39 (25)	39 (54)	39 (68)	39 (20)	39 (44)

[a]The relative intensity unknown (two fragment ions at the same *m/z* value).

α-hydrogens, we had to estimate the ratio **8a** : **8b** from the poorley separated GC peaks to be about 90 : 10.

Mechanistic consideration of BrCl *addition*

If the first step in these bromine chloride additions is assumed to be the bromonium ion formation, the varying regioisomer proportions might point to the facts that can effect on the direction of the ring opening of these bromonium ions.

Heasley *et al.*[3] considered two possible effects that the carbonyl group may exert on the direction of the ring opening of a neighbouring bromonium ion. If it shows S_N2 character, increased α attack of the nucleophile (chloride ion) would be expected, as S_N2 displacements are accelerated by an adjacent carbonyl group.[6] If, on the other hand, the mechanism was S_N1, the positive carbonyl carbon should discourage the carbocation formation at the α carbon and thereby decrease the α attack of the nucleophile.

If S_N1 mechanism is assumed in our case, the methyl group in methyl 2-methyl-2-butenoate **2** would stabilize positive charge on C-2 and increase α attack compared to methyl crotonate **1**. Opposite is, however, observed. The greater the contribution of the polar canonical form, $C^{+}-O^{-}$, is, the less evident is the carbocation formation on C-2. Table 3 shows that the derivatives of **2** exhibit the carbonyl carbon resonances at about 1.6 ppm lower field than the derivatives of **1** and **3**, like the parent 2-methyl-2-butenoic and 2-methylbutanoic acids. Hence, the more positive carbonyl carbon in **2** might discourage an S_N1-type α attack. The difference in the carbonyl carbon resonance may, however, be negligible to be indicative of increased polarity of the carbonyl double bond. Actually, steric hindrance to the ring opening at the α-position seems a more obvious explanation, which would favour an S_N2-type mechanism; without an accelerating influence of an adjacent carbonyl group, no nucleophilic attack would occur at this position.

Similarly the methyl group in **3** would increase an S_N1-type β attack compared to **1** by stabilizing the positive charge on C-3. Actually **3** shows most β attack, even more than methyl isocrotonate of Heasley *et al.*[3]

Table 2. ^{1}H NMR data of some halogenated methyl butanoates.

Methyl butanoate	Chemical shifts (ppm), multiplicity[a], J (Hz)
4 2,3-Di-Cl	3.77 (s, 3H); 4.11 (c, 1H); 4.26 (c, 1H); 1.64 (d, 3H)
6 2,3-Di-Br	3.77 (s, 3H); 4.04-4.65 (c, 2H); 1.88 (d, 3H)
7 2,3-Di-Cl-2-Me	3.81 (s, 3H); 4.60 (q, 1H, J≈6.6); 1.74 (s, 3H); 1.63 (d, 3H, J≈6.6)
9 2,3-Di-Br-2-Me	3.82 (s, 3H); 4.83 (q, 1H, J≈6.6); 1.95 (s, 3H); 1.89 (d, 3H, J≈6.6)
10 2,3-Di-Cl-3-Me	3.77 (s, 3H); 4.35 (s, 1H); 1.78 (s, 3H); 1.74 (s, 3H)
12 2,3-Di-Br-3-Me	3.77 (s, 3H); 4.57 (s, 1H); 2.01 (s, 3H); 1.92 (s, 3H)
11a 2-Br-3-Cl-3-Me	3.77 (s, 3H); 4.42 (s, 1H); 1.87 (s, 3H); 1.78 (s, 3H)

[a]s, singlet; d, doublet; q, quartet; c, complex absorption.

Table 3. ^{13}C shifts data for halogenated methyl butanoates.

Methyl butanoate	Chemical shifts (ppm)						
	C-1	C-2	C-3	C-4	OCH_3	2-CH_3	3-CH_3
4 2,3-Di-Cl	166.5	59.9	54.9	21.2	52.4		
6 2,3-Di-Br	166.7	48.7[a]	44.9[a]	23.6	52.4		
5a 2-Br-3-Cl	166.6	48.6	54.9	22.5	52.5		
5b 3-Br-2-Cl	166.6	60.0	45.1	22.2	52.5		
7 2,3-Di-Cl-2-Me	168.2	68.8	59.3	18.7	52.7	20.0	
9 2,3-Di-Br-2-Me	168.2	61.3	51.2	20.6	52.7	21.0	
8a 2-Br-3-Cl-2-Me	168.3	61.0	59.5	19.5	52.6	20.3	
8b 3-Br-2-Cl-2-Me	168.0	68.8	50.8	19.7	52.6	20.6	
12 2,3-Di-Br-3-Me	166.5	53.4	60.9	33.6	52.1		28.0
11a 2-Br-3-Cl-3-Me	166.6	52.9	67.1	31.5	52.1		26.9
10 2,3-Di-Cl-3-Me	166.3	68.4	63.2	30.4	52.0		26.5

[a]The shifts are reversed in Ref. 8.

The fact that methyl crotonate shows less β attack than methyl acrylate, could arise according to them from increased steric hindrance by the methyl group, forcing the chloride ion to attack the α-carbon. Then still more α attack, however, would be expected from **3**; observed α attack is few per cent. The opening of the bromonium ion from **3** seems to support an S_N1-type mechanism. Heasley *et al.*[3] accounted the great increase of β attack in the bromonium ion from methyl isocrotonate compared to that from methyl crotonate by an unsymmetrically bridged bromonium ion with considerable positive charge on the β-carbon, caused by the steric interference of the eclipsed methyl and carbomethoxy groups. The chloride ion would then attack β-carbon by an S_N1-type reaction. The almost quantitative β attack to **3** could be explained similarly.

Identification of products by mass, ^{1}H *and* ^{13}C NMR *spectrometry*

The characteristic mass spectral fragment ions of the major halogenation products of methyl butenoates are presented in Table 1. Fig. 2 gives the mass spectrum of erythro methyl 2,3-dichlorobutanoate **4**. The molecular ion peaks of compounds are small and not shown in the spectra. α-Cleavage produces $(M\text{-}OCH_3)^+$ and $(M\text{-}COOCH_3)^+$ ions. The former are weak owing to the electronegative halogen atom at the 2-position,[7] the intensities of the latter being at greatest in the case of chloro compounds **4**, **7**, **10**. The β-cleavage and the McLafferty rearrangement produce ions in appreciable abundance in **4**, **7**, **10** and **11a**, **11b**. The loss of a halogen atom from the molecular ion gives intense peaks, particularly in the case of bromo compounds. Judging from the mass spectra of monochloro esters,[7] the elimination of chlorine occurs practically from the 3-position. The bromine substituent, evidently, owing to its greater atomic weight is, however, eliminated from the 2-position in the bromochloro isomers **5a**, **5b**; **8a**, **8b** and **11a**, **11b**. The elimination of hydrogen halide from the molecular ion gives always weaker peaks than the loss of a halogen atom, the $(M\text{-}HX)^{+\cdot}$ fragment ion being shown only in **4** and **7**. α-Cleavage and the loss of a halogen atom produce together the $(M\text{-}X\text{-}COOCH_3)^{+\cdot}$ peaks, intense in the spectra of chloro esters (base peak in **4** and **7**). In addition, the subsequent loss of another halogen atom gives the $C_3H_5^+$ and $C_4H_7^+$ fragment ions at *m/z* 41 and 55, respectively (base peaks in most compounds).

^{1}H NMR data are given in Table 2. The data from the regioisomer mixtures **5a**, **5b** and **8a**, **8b** are not included in Table 2 due to the complexity of the spectra. ^{1}H NMR shifts of erythro methyl 2,3-dichlorobutanoate **4** are from our previous paper.[2]

The ^{13}C shifts for the dihalo compounds are given in Table 3. According to Velichko *et al.*[8] C-3 resonance in erythro methyl 2,3-dibromobutanoate **6** appears lower field from C-2 resonance. We are, however, on the basis of our experience on the corresponding chloro esters, disposed to believe the opposite order of these resonances. The differences in the ^{13}C shifts between ours and those reported are evidently due to the different solvent and concentrations (Ref. 8: 19:1 compound/chloroform). Comparison of the effects of chlorine and bromine on the shifts of the substituted carbons shows that the position of the methyl group has a greater effect on C-2 and C-3 shifts than variation of the vicinal halogen substituent (chlorine or bromine on C-3 and C-2, respectively). This is, of course, due to the generally known fact that β effects of chlorine and bromine are practically the same.[9]

Acknowledgement—I. Korhonen wishes to express his gratitude to the Academy of Finland for financial support.

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