Whereas in experiments with all substrates but **1e** the value of k_{ArI}/k_{PhBr} reckoned from each aliquot varied randomly within a run, as illustrated in Table IV, a different pattern of behavior was encountered with **1e**. One of two nearly identical experiments is detailed in Table V. It should be noted that bromide ion release nearly ceased after 3 min. In the other experiment, the value of k_{ArI}/k_{PhBr} for the initial aliquot was 13.4. The average of 11.4 (Table V) and 13.4 is 12.4, and this was multiplied by the fraction of **3e** in the product mixture of **3e** and **4** to get the value of k_{ArI}/k_{PhBr} for the $S_{RN}1$ reaction of **1e** listed in Table II.

(14) Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; p 159.

Registry No. 1a, 591-50-4; **1b**, 624-31-7; **1c**, 625-95-6; **1d**, 696-62-8; **1e**, 766-85-8; **1f**, 352-34-1; **2**, 51742-96-2; **3a**, 6721-67-1; **3b**, 61394-79-4; **3c**, 61394-80-7; **3d**, 65853-51-2; **3e**, 61394-81-8; **3f**, 70445-94-2; **4**, 33617-66-2; bromobenzene, 108-86-1.

Considerations on the Effect of a Carbonyl Group on the Ring Opening of a Neighboring Bromonium Ion

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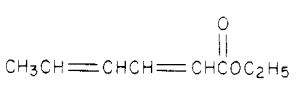
Studies on the addition of bromine chloride (BrCl) to methyl acrylate (**3a**), methyl isocrotonate (**3b**), and methyl crotonate (**3c**) under ionic and radical conditions are reported. Under ionic conditions, the following percentages of α attack (adjacent to carbonyl group) of the chloride ion on the intermediate bromonium ions to give bromo chlorides occurred respectively: **3a** (17%), **3b** (7%), and **3c** (8%). On the basis of these results, we conclude that the carbonyl group in the bromonium ions for **3a–c** does not accelerate ring opening at the α position as might be anticipated if the ring openings occurred by an S_N2 process. On the other hand, an S_N1 mechanism in these ring openings is not supported by the results from **3c**. More β attack should occur with **3c** than **3a** if the mechanism is S_N1 since the methyl group should stabilize development of a positive charge at the β carbon. Perhaps the ring openings occur by an S_N2 process, but the carbonyl group fails to accelerate α attack because the essential orbitals do not align properly with the π bond of the carbonyl group. Radical addition of BrCl to **3a** produced exclusively methyl 3-bromo-2-chloropropionate. Apparently, the bromine atom attacks the β carbon to give a resonance-stabilized intermediate which abstracts a chlorine atom from BrCl. The ionic reactions of BrCl with **3b,c** are so rapid that there appears to be little radical addition in these cases.

During recent investigations of ours[1,2] on the halogenation of ethyl sorbate (**1**), we became interested in the effect that the carbonyl group exerts on the direction of ring opening of a neighboring bromonium ion (**2**). The literature contains numerous references to studies on the first step in halogenation reactions (halonium ion formation), but there have been few investigations of factors which influence the direction of halonium ion ring openings (the second step).

When we began our study, the only previous investigation in this area was done by de la Mare and coworkers[3a-c] on the addition of hypochlorous acid and chlorine acetate to cinnamic acid and methyl cinnamates. In these reactions, the chloronium ion was opened exclusively at the carbon adjacent to the phenyl ring. These investigators also determined the kinetics of the addition of chlorine acetate to acrylic acid but did not establish the composition of the product. They did state, however, that, "It is interesting to note, however, that the reaction does not appear to be completely regiospecific...".[3c] Recently, Dubois and Chretien discussed the ring openings of bromonium ions from the standpoints of charge distribution in the bromonium ion and hard–soft acid–base theory.[4]



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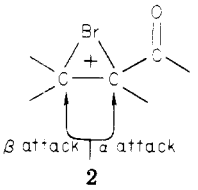

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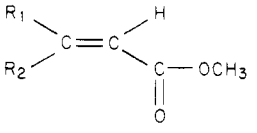
We choose to study the addition of bromine chloride, BrCl, in methylene chloride to the following carbonyl conjugated olefins: methyl acrylate (**3a**), methyl isocrotonate (**3b**), and methyl crotonate (**3c**). To the best of our knowledge, BrCl or other unsymmetrical electrophiles have not been added to **3a–c** or closely related alkenes under the conditions described in this paper.[5]



3a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = H$

(1) D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **42**, 2141 (1977).
(2) D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **43**, 2652 (1978).
(3) (a) P. B. D. de la Mare and M. A. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 653 (1973); (b) P. B. D. de la Mare, M. A. Wilson, and M. J. Rosser, *ibid.*, 1480 (1973); (c) P. B. D. de la Mare, C. J. O'Connor, and M. A. Wilson, *ibid.*, 1150 (1975).
(4) J. E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100**, 3506 (1978).
(5) Bromine chloride in aqueous solution, prepared in situ from $KBrO_3$, KBr, and 25% HCl, was added to acrylic acid and *n*-butyl methacrylate. Only anti-Markownikov addition (β attack) was reported: S. Groszkowski and J. Sienkiewicz, *Rocz. Chem.*, **45** (10) 1779 (1971). P. Melikoff (*Ber.*, **12**, 2227 (1879); **13**, 2153 (1880)) reported that 2-chloro-3-hydroxypropanoic acid and 3-chloro-2-hydroxypropanoic acid are formed in the addition of HOCl to acrylic acid.

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At least two effects of a carbonyl group can be imagined. It is well known that S_N2 displacements are greatly accelerated by an adjacent carbonyl group.[6] So, if there is S_N2 character in the opening of a bromonium ion, α attack should be accelerated by the adjacent carbonyl. On the other hand, the positive carbonyl carbon should discourage carbocation formation at the α carbon and thereby decrease the attack by the nucleophile at the α carbon if the reaction proceeds by an S_N1 mechanism.

Results

Addition of BrCl to methyl acrylate (**3a**) under ionic conditions gave primarily anti-Markownikov product (β attack, **5**):

$$\mathbf{3a} \xrightarrow[CH_2Cl_2]{BrCl} \underset{\mathbf{5}\ (83\%)}{CH_2(Cl)CH(Br)C(O)OCH_3} + \underset{\mathbf{6}\ (17\%)}{CH_2(Br)CH(Cl)C(O)OCH_3}$$

Methyl isocrotonate (**3b**) reacted with BrCl to give less α attack than **3a**, whereas methyl crotonate (**3c**) gave more:

$$\mathbf{3b} \xrightarrow[CH_2Cl_2]{BrCl} \underset{\mathbf{7}\ (93\%)}{CH_3CH(Cl)CH(Br)C(O)OCH_3} + \underset{\mathbf{8}\ (7\%)}{CH_3CH(Br)CH(Cl)C(O)OCH_3}$$

$$\mathbf{3c} \xrightarrow[CH_2Cl_2]{BrCl} \mathbf{7}\ (70\%) + \mathbf{8}\ (30\%)$$

Bromochloride regioisomers **5** and **6** (also **7** and **8**) could not be separated by VPC analysis. NMR analysis of the two mixtures of isomers gave spectra which were consistent with the proposed structures, but the analysis could not be used to determine the percentage of each regioisomer in the mixtures.

Instead, the bromochlorides were analyzed by conversion to eliminate products. We had already established in our studies[1] on the 1,4-dihalides of ethyl sorbate that eliminations with triethylamine were initiated exclusively by attack of the base on the acidic α-hydrogen. Therefore we assumed, and in fact showed, that bromochlorides from **3a–c** would eliminate in an analogous manner.

$$\underset{\begin{array}{l}\mathbf{6},\ R_1 = R_2 = H\\ \mathbf{8},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C(Br)CH(Cl)C(O)OCH_3} \xrightarrow{(CH_3CH_2)_3N} \underset{\begin{array}{c}\mathbf{9},\ R_1 = R_2 = H\\ \mathbf{10},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C{=}C(Cl)C(O)OCH_3}$$

$$\underset{\begin{array}{l}\mathbf{5},\ R_1 = R_2 = H\\ \mathbf{7},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C(Cl)CH(Br)C(O)OCH_3} \xrightarrow{(CH_3CH_2)_3N} \underset{\begin{array}{c}\mathbf{11},\ R_1 = R_2 = H\\ \mathbf{12},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C{=}C(Br)C(O)OCH_3}$$

The authentic elimination products were synthesized from the appropriate dihalide. Compounds **9**, **10**, **11**, and **12** were isolated by preparative VPC. The structures of **9**, **10**, and **12** were established by NMR analysis except for the stereochemistry of **10** and **12**. The NMR spectra did confirm that these compounds were not mixtures of *E,Z* isomers. We assumed that **10** and **12** have the *E* configuration because the steric hindrance would be greatest if the halogen and the methyl group were cis.

$$\underset{\begin{array}{l}\mathbf{13},\ R_1 = R_2 = H\\ \mathbf{14},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C(Br)CH(Br)C(O)OCH_3} \xrightarrow{(CH_3CH_2)_3N} \underset{\begin{array}{c}\mathbf{15},\ R_1 = R_2 = H\\ \mathbf{16},\ R_1 = CH_3;\ R_2 = H\end{array}}{R_1R_2C(Cl)CH(Cl)C(O)OCH_3} \xrightarrow{(CH_3CH_2)_3N}$$

11 (from **13**) and **12** (from **14**)

9 (from **15**) and **10** (from **16**)

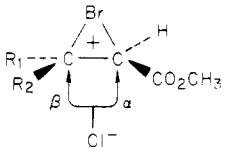
Markownikov addition to form **6** occurred exclusively when BrCl reacted with **3a** in the presence of ultraviolet irradiation (a radical addition):

$$\mathbf{3a} + BrCl \xrightarrow{h\nu} \mathbf{6}\ (100\%)$$

Radical additions of BrCl to **3b** and **3c** gave ratios of regioisomers (**7** and **8**) which were similar to those from ionic additions, although there was a greater loss in stereospecificity.

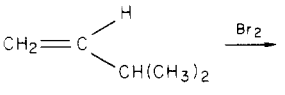
Discussion

The small amount of **6** that is formed in the reaction of methyl acrylate (**3a**) with BrCl suggests that α attack of chloride in **17a** is not accelerated by the adjacent carbonyl



17a, $R_1 = R_2 = H$
b, $R_1 = H_1$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_1 = H$

group. On the other hand, one might argue that the steric hindrance at the α carbon in **17a** is so severe that no ring opening would occur at this position were it not for the accelerating influence of the carbonyl group. We doubt that the steric hindrance is that significant. The degree of steric hindrance in the bromonium ion (**19**) from 3-methyl-1-butene (**18**) may serve as a model for **17a**. Although BrCl has not been added to **18**, Br_2 in CH_3OH has,[7] and the amount of Markownikov ring opening is significant.[8]



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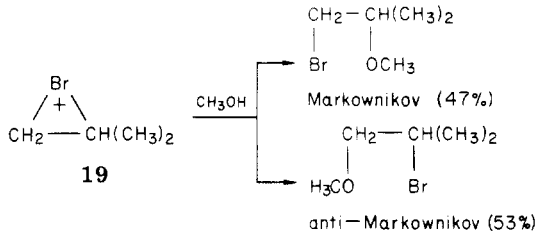

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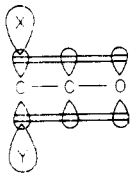
Conceivably, the carbonyl group fails to accelerate ring opening because of misalignment of orbitals. In order for S_N2 displacement to be accelerated by a neighboring carbonyl group, several orbitals must be aligned correctly: the orbitals composed of the nucleophile, the leaving group,

(6) E. S. Gould, "Mechanisms and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, 1959, p 284.

(7) M. Lafosse and M. Savignac, *Chromatographic*, **6** (10), 415 (1973).

(8) Although CH_3OH is a much more polar solvent than the CH_2Cl_2 used in this study, the amounts of Markownikov-anti-Markownikov products, respectively, were not found to differ markedly in additions of BrCl to 1-hexene in CCl_4 (61%:39%) and CH_3OH (51%:49%). The Markownikov-anti-Markownikov ratio of methoxy bromides was determined to be 67%:33%. (See: V. L. Heasley, D. F. Shellhamer, J. A. Iskikian, and D. L. Street, *J. Org. Chem.*, **43**, 3139 (1978)).

and the α carbon must overlap with the π bond of the carbonyl (**20**). In the ring opening of **17a**, the bond to the



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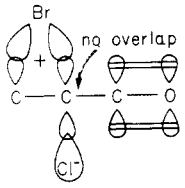

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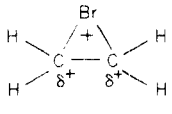
leaving group is bent toward the halogen and may not be sufficiently close for overlap with the carbonyl group, resulting in no acceleration. It would be helpful to know how an epoxide adjacent to a carbonyl group is opened under Sn_N2 conditions, but the old literature in this area can give no assurance of S_N2 conditions or kinetically controlled products.

Does the failure to observe acceleration mean that the ring opening in **17a** is occurring by an S_N1 process? Not necessarily. Consider the ring opening of **17c** from methyl crotonate (**3c**): If the ring opening in **17a** were occurring by an S_N1 process, there would be greater β attack in **17c** than in **17a** because the methyl group should stabilize development of a positive charge at the β carbon.[9] Actually, the data show that there is less β attack in **17c** which we interpret as arising from increased steric hindrance by the methyl group, forcing the chloride ion to attack at the α-carbon. Failure to observe an increase in β attack in **3c** compared to **3a** supports an S_N2-type mechanism in these ring openings.

Returning to another consideration in the ring opening in **17a**, we believe that the extent of β attack in **17a** is greater than can be accounted for on the basis of the steric effect of the carbonyl group. The research of Olah and co-workers[9] suggests that the carbon atoms in the bromonium ion from ethylene (**22**) bear some positive charge,



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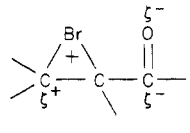

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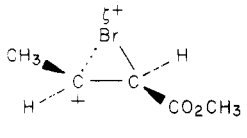
with the principal charge on bromine. In the case of **17a**, the carbonyl group should destabilize the positive charge at the α-carbon more than at the β-carbon (**23**). Perhaps the chloride ion prefers to attack at the positive β-carbon, although the data from the opening of **17c** suggest that the positive charge on the β-carbon is insufficient to cause the ring opening to occur by an S_N1 process.

The great increase in β-attack by the chloride ion in the bromonium ion **17b** from methyl isocrotonate **3b** compared to **17c** from methyl crotonate may be accounted for in the following manner: Due to steric interference, the eclipsed methyl and carbomethoxy groups are forced out of the plane resulting in an unsymmetrically bridged bromonium ion (**24**) with considerable positive charge on the β-carbon



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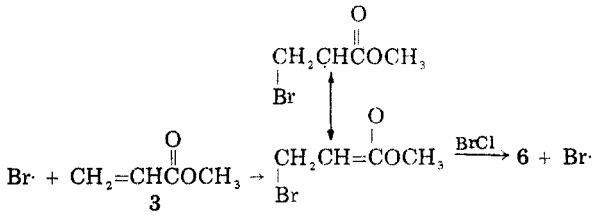
and little charge on bromine. The chloride ion can now attack the carbocation-like β-carbon in an S_N1-type reaction.

Finally, let us consider the radical addition of BrCl to methyl acrylate (**3a**). Apparently, the bromine atom attacks the β-carbon of **3** to give a resonance-stabilized intermediate radical which continues the chain reaction by attacking BrCl producing **6** and another bromine atom:



Br_2 and Cl_2 as well as BrCl may be involved in the photoaddition process since they are known to exist in equilibrium in small amounts with BrCl.

We conclude that additions of BrCl to **3bc** under radical conditions are probably proceeding primarily by an ionic mechanism since the ionic reactions of **3bc** and BrCl are extremely rapid and because the stereospecificity of the addition is greater than would be expected from a radical addition.

Experimental Section

Materials. All solvents and reagents were obtained commercially in high purity and were used without further purification. Bromine chloride was prepared by adding an equimolar amount of bromine to a chlorine–methylene chloride solution (0.5–1.0 M). Methyl isocrotonate (**3b**) was synthesized from isocrotonic acid[10] by the following procedure: To 2 g (23.2 mmol) of isocrotonic acid in 40 mL of acetone in a flask equipped with a reflux condenser and a magnetic stirrer was added 1.76 g (12.7 mmol) of anhydrous potassium carbonate. Following neutralization, 5.0 g (34.7 mmol) of methyl iodide was added. The reaction mixture was stirred for several hours, and then the solid potassium iodide was removed by centrifugation. Following removal of the acetone, vacuum distillation (55–60 °C (110 mm)) gave 0.87 g (38%). The structure of **3b** was confirmed by its NMR and IR spectra (CCl_4): δ 2.11 (d, 3 H, J = 1.4 and 6.8 Hz), 3.62 (s, 3 H), 5.68 (d, 1 H, J = 11.2 and 1.4 Hz), 5.98–6.54 (m, 1 H, J = 11.2 and 6.8 Hz); C=O and C=C (conjunction), 1715 and 1630 cm^{-1}, respectively. VPC and NMR analyses confirmed that **3b** contained no **3c**.

Reaction of Methyl Acrylate (3a), Methyl Isocrotonate (3b), and Methyl Crotonate (3c) with the Halogens. General Procedure. To 6.4 mmol of each ester (**3a–c**) in 20 mL of CH_2Cl_2 (0.02 mol fraction) was added 1.6 mmol of halogen. (Bromine was added neat, and bromine chloride and chlorine were added as ca. 1.2 M solutions in CH_2Cl_2.) The mixtures were stirred briefly and allowed to stand until the reactions were complete. The solvent was removed under reduced pressure.

The yields of some of the addition products are: **3a** with BrCl, 89%; **3b** with BrCl, 85%; **3c** with BrCl, 91%. The yields were obtained by NMR using benzene as an internal standard.

Dehydrohalogenation of the Dihalo Esters (13, 15, 5, 6, and 14, 16, 7, 8) with Triethylamine. General Procedure. To 2 mmol of dihalide in 25 mL of pentane was added 10 mmol of triethylamine. The reaction mixtures were allowed to stand at room temperature until they were determined to be complete by VPC analysis. Approximate time required for completion: dihalides from **3a**, 10 h; dihalides from **3b,c**, 48 h. The amine was removed from the pentane solution by extraction with 1 M HCl. Elimination products **11**, **9**, **12**, and **10** were isolated by preparative VPC.

The yields of some of the elimination products are: **9** and **11** from **5** and **6**, 95%; **10** and **12** from **7** and **8** (from **3b** and **3c**), 85%. The yields were obtained by NMR using benzene as an internal standard.

(9) Olah has shown that the positive charge is located significantly on the substituted carbon in the bromonium ion form 1-propene: G. A. Olah, "Halonium Ions", Wiley, New York, 1975, p 114.

(10) C. Rappe, *Acta Chem. Scand.*, 17, 2766 (1963).

Table I. Physical Data of the Compounds

compd	NMR, ppm	IR, cm^{-1} C=C	IR, cm^{-1} C=O	bp, °C (mm)
5 and 6	δ 3.6-4.5 (m, 3 H), 3.83 (s, 3 H)	*a*	1754	*b*
7 and 8	δ 1.74 (d, 3 H), 3.80 (s, 3 H), 4.0-4.5 (m, 2 H)	*a*	1752	*b*
9	δ 3.83 (s, 3 H), 5.93 (d, 1 H, J = 1.4 Hz), 6.50 (d, 1 H, J = 1.4 Hz)	1616	1725	*b*
10	δ 1.92 (d, 3 H, J = 6.8 Hz), 3.77 (s, 3 H), 6.9-7.3 (q, 1 H, J = 6.8 Hz)	1630	1719	*b*
11	δ 3.83 (s, 3 H), 6.13 (d, 1 H, J = 1.2 Hz), 6.87 (d, 1 H, J = 1.2 Hz)	1613	1723	*b*
12	δ 1.96 (d, 3 H, J = 6.6 Hz), 3.78 (s, 3 H), 7.1-7.5 (q, 1 H, J = 6.6 Hz)	1623	1716	*b*
13	δ 3.4-4.5 (m, 3 H), 3.83 (s, 3 H)	*a*	1753	95-97 (28)
14	δ 1.87 (d, 3 H), 3.80 (s, 3 H), 4.2-4.6 (m, 2 H)	*a*	1750	63-66 (0.1)
15	δ 3.6-4.5 (m, 3 H), 3.83 (s, 3 H)	*a*	1750	73-75 (28)
16	δ 1.66 (d, 3 H), 3.80 (s, 3 H), 4.0-4.4 (m, 2 H)	*a*	1755	67-69 (2.5)

[a] Double bond is not conjugated and therefore weak. [b] Compounds were isolated by preparative VPC, and the boiling points were not determined.

Isolation of the Products. Dihalides **13**, **15**, **14**, and **16** were isolated by vacuum distillation (see Table I for boiling point data).

Preparative VPC was used to obtain pure **5** and **6**: 85 °C on a column (SS, 10 ft. × 0.25 in.) packed with 5% SE-30 on 80–100 Chromosorb W. Dibromide **13** and dichloride **15** were also analyzed under the same conditions. Retention times (min) are: **5**, **6** (4.7), **13** (7.7), and **15** (2.5).

Pure **7** and **8** were isolated by preparative VPC: 85 °C on a column (SS, 5 ft. × 0.25 in.) packed with 2.5% SE-30 on 80–100 Chromosorb W. Dibromide **14** and dichloride **16** were analyzed on the same column. Retention times (min) are: **7** and **8** (7.2 and 9.4, diastereomers), **14** (13.4), and **16** (4.5).

Elimination products **9**, **10**, **11**, and **12** were isolated by preparative VPC. VPC analysis at 100 °C on a column (SS, 10 ft × 0.25 in.) packed with 2.5% SE-30 on 80–100 Chromosorb W gave the following retention times (min): **11** (2.1), **9** (1.6), **12** (5.9), and **10** (3.5).

Discussion of the VPC Analysis of the Bromochloride Products from the Addition of BrCl to 3b and 3c. Analysis of the bromochloride product from **3b** showed two peaks whose retention times were identical with peaks from the bromochloride product from **3c**. We conclude, based on the following pieces of evidence, that the compounds responsible for the peaks are diastereomers and not regioisomers: (a) the relative percentages of the peaks are in line with what would be expected for the stereospecificities of addition of BrCl to **3b** and **3c**, respectively [peak 1 (98%, 10%) and peak 2 (2%, 90%)]; (b) the percentages of peaks 1 and 2 do not agree with the percentages of **10** and **12**; and (c) we were unable to separate regioisomers **5** and **6** by VPC analysis, and, furthermore, all attempts to separate the regioisomeric 1,4-bromochlorides from addition of BrCl to piperylene failed.[11]

Since regioisomers **7** and **8** from **3b** are apparently diastereomers[12] of **7** and **8** from **3c**, we were surprised that the NMR spectrum of **10** and **12** from elimination of the former mixture was identical with the spectrum of the elimination product of the latter mixture; stereospecific eliminations of the mixtures should give *E* isomers from the former and *Z* isomers from the latter. There are at least two possible explanations for the fact that both eliminations give only a single type of isomer (probably the *E* isomer): (a) the elimination proceeds by a carbanion-type mechanism, because of the stabilizing effect of the carbonyl group, and the stereochemistry is lost by inversion of the carbanion; and (b) the amine (an excess is present) adds reversibly to the *Z* isomers of **10** and **12** by a Michael-type addition converting them to **10** and **12** with *E* geometry. We proved that the first explanation is not correct by confirming that regioisomers **7** and **8** from **3b** and **3c** are not interconverted in the presence of amine. We were unable to test the second explanation since the *Z* isomers of **10** and **12** were not available.

Proof for the Structures of the Compounds. The proof for the structures of the compounds in this study is based primarily on the physical data presented in Table I. The NMR and IR (C=O) data are consistent with all proposed structures, as are the IR (C=C) and boiling point data where applicable. An important further proof for the structures of **5** and **6**, **7** and **8**, **13**, **14**, **15**, and **16** is that these compounds undergo elimination to give elimination compounds **9**, **10**, **11**, and **12** whose structures are indisputably established by NMR and IR data.

Reaction of Methyl Acrylate (3) with Bromine Chloride in the Presence of Ultraviolet Irradiation. To neat methyl acrylate (**3**) under irradiation with a sunlamp and maintained at room temperature was added sufficient BrCl to react with 5% of the alkene. The reaction was complete in 3 min. The mixture of **5** and **6** was isolated by preparative VPC and analyzed as described above.

Are the Reactions of 3a–c and BrCl Occurring by An Ionic Reaction? We have taken all precautions to avoid a molecule–homolytic radical reaction: the halogenations have been done in the dark and in dilute solutions. The chances of a concomitant radical reaction with **3b,c** and BrCl are very unlikely since these reactions are extremely rapid and are nearly stereospecific. We also established that the ratios of diastereomers of **7** and **8** from both **3b** and **3c** were not changed when the radical inhibitor isoamyl nitrite was added. The reaction of **3a** and BrCl is much slower than **3b,c**, and the possibility of a concomitant radical reaction is greater. We cannot absolutely be certain that a radical reaction is not occurring. However, if some bromochloride **6** is formed by a radical reaction, it would mean that **19a** is undergoing less than the reported 17% α attack which is even more interesting vis-à-vis the openings of **3b,c**.

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Registry No. 3a, 96-33-3; **3b**, 4358-59-2; **3c**, 623-43-8; **5**, 67280-57-3; **6**, 67280-59-5; **7**, 70288-52-7; **8**, 70288-53-8; **9**, 80-63-7; **10**, 22038-57-9; **11**, 4519-46-4; **12**, 36297-23-1; **13**, 1729-67-5; **14**, 5469-24-9; **15**, 3674-09-7; **16**, 54460-97-8; BrCl, 13863-41-7; isocrotonic acid, 503-64-0.

(11) G. E. Heasley, J. M. Bundy, V. L. Heasley, S. Arnold, A. Gipe, D. McKee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *J. Org. Chem.*, **43**, 2793 (1978).

(12) As we have stated, regioisomers **7** and **8** from **3b** are contaminated with a small amount of the diastereomers of regioisomers **7** and **8** from **3c** and vice versa.