at the failure of diagram 2 on p 122 to specify whether the rotation of amine or amine hydrochloride was meant, we repeated their correlation of configuration. We find that if the diagram refers to amine salt, the data of ref 21 are internally consistent and in accord with those in ref 18. We have only given rotations for neat amine, whose sign of rotation is opposite to that of its hydrochloride.

(22) W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).
(23) (a) R. D. Guthrie, *J. Am. Chem. Soc.*, **89**, 6718 (1967); (b) H. S. Mosher, *Tetrahedron*, **30**, 1733 (1974).
(24) R. A. Moss and D. W. Reger, *J. Am. Chem. Soc.*, **91**, 7539 (1969).
(25) R. A. Moss, C. J. Talkowski, D. W. Reger, and C. E. Powell, *J. Am. Chem. Soc.*, **95**, 5215 (1973).
(26) K. B. Wiberg, Ph.D. Thesis, Columbia University, New York, N.Y., 1950.
(27) A. J. Finlayson and C. C. Lee, *Can. J. Chem.*, **37**, 940 (1959).
(28) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).
(29) G. M. Kramer, *J. Am. Chem. Soc.*, **91**, 4819 (1969); **92**, 4344 (1970).
(30) Yu. G. Bundel, I. Yu. Levina, I. R. Prokhorenko, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **188**, 348 (1969).
(31) C. H. DePuy, A. H. Andrist, and P. C. Fünfschillin, *J. Am. Chem. Soc.*, **96**, 948 (1974).
(32) The fact that 14% active *erythro*- and 6% active *threo*-3-phenyl-2-butyl acetate are produced by acetic acid deamination of optically active *threo*-3-phenyl-2-aminobutane lends some credence to this hypothesis. See D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).
(33) Deamination of optically active 2-methyl-1-aminobutane gives 2-pentanol with 38% net inversion. See W. Kirmse and H. Arold, *Chem. Ber.*, **103**, 23 (1970).
(34) L. D. McManus and N. A. J. Rogers [*Tetrahedron Lett.*, 4735 (1969)] have reported rapid equilibration between edge-protonated cyclopropane derivatives in aqueous solution.
(35) No attempt will be made to distinguish between partial equilibration of **5a** with **5b** and **6a** with **6b** and initial formation of **5a, 6a** with subsequent isomerization to **1,2**.
(36) Other protonated cyclopropane intermediates are responsible for the partial racemization of the isolated 2-methyl-1-butanol (ref 33).

Thermal Fragmentation of β-Halo Esters via Chain Halogenolysis–Decarboxylation–Elimination[1]

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Solution pyrolysis (240°) of dimethyl 1,2-dibromocyclobutane-1,2-dicarboxylate gives CO_2 and methyl bromide (2 mol) in good yield in lieu of cracking or geometrical isomerization. According to their behavior under pyrolysis conditions, methyl 3-bromocyclobutene-2-carboxylate and methyl 3-bromobutadiene-2-carboxylate are permissible intermediates in the cyclobutane decomposition. Elimination–debromocarbomethoxylation of β-halo esters appears to be quite general since derivatives of the methyl 3-halopropenoates and methyl 3-bromopropanoate also decompose to CO_2 and methyl halide at elevated temperatures. Elimination products, unstable under high temperature pyrolysis conditions, are not obtained in significant yield. The kinetics for these fragmentations appear complex, exhibiting in some cases autocatalytic behavior. Substituent and solvent effect data and the results of gas phase decomposition rule out pericyclic or ion pair mechanistic possibilities. The effects of additives on the course of pyrolysis reveal that a chain decomposition is important, more likely involving halide ion displacement on the ester group followed by decarboxylation–elimination than a similar free-radical chain mechanism. Catalysis of halo ester fragmentation by halide ion is quite effective, and in some cases moderate yields of elimination product are obtained. The use of halogenolysis–decarboxylation–elimination in synthetic and degradative schemes is discussed.

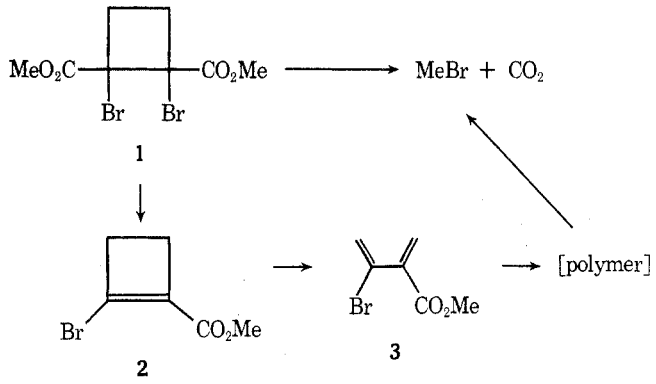
In search for heavy-atom effects in thermal reactions which in principle involve diradicals, we have examined the pyrolysis of halogen substituted cyclobutanes. In one series a surprising fragmentation took place in lieu of expected ring opening. We report now the generality of this halogenolytic degradation of β-halo esters along with data that suggest a mechanism.

Results and Discussion

Neither cracking to methyl 2-bromopropenoate nor geometrical isomerization[2] were observed on static pyrolysis of the stereoisomeric dimethyl 1,2-dibromo-1,2-cyclobutanedicarboxylates (**1**)[3] in diphenyl ether (DPE), diphenylmethane (DPM), or nitrobenzene (NB). Decomposition at 240° produced in nearly quantitative yield methyl bromide (2 mol), identified by GLC and NMR comparison with authentic material. No other volatile organic material was obtained in significant amount, but CO_2 (60% of the theoretical 2 mol) was trapped from pyrolysis solutions using Ascarite.

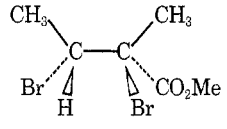
Cyclobutene **2**, the product of a suspected eliminative debromocarbomethoxylation of **1**, was prepared independently and pyrolyzed. At 160° smooth first-order ring opening to **3** ($k = 5.1 \times 10^{-4}$ sec^{-1}) occurred, followed by slow decomposition to nonvolatile, presumably polymeric material. Butadiene **3** from preparative GLC of a pyrolysate of **2** polymerized as a neat sample at room temperature. Characterization involved ir, NMR, and tandem VPC–mass spectral analysis of a CCl_4 solution of **3** obtained by collection of a GLC injector port pyrolysis of **2**. Remarkably, heating a sample of **2**, after ring opening at 160°, briefly at 240° gave methyl bromide and CO_2.

With the novel eliminative degradation of **1** a strong possibility, we examined other halo esters expecting that the fragmentation might be general. Indeed, solution pyrolysis of **4–7** gave methyl bromide and CO_2 (about 60% each). The halomaleates, obtained from commercially available bromo- and chloromaleic anhydride, were the starting materials for **4–6**. Preequilibrium of maleates and fumarates (about 40:60), which was rapidly established at the onset temperatures for fragmentation to methyl bromide (300, 290, and 250°, respectively), was indicated by GLC and the appearance in the NMR of new signals assignable to olefinic (lower field for the fumarates) and OMe resonances. Dimethyl bromofumarate (**5**),[4] obtained by preparative GLC of a partial pyrolysate, was identified from spectral data and pyrolyzed separately. Brief pyrolysis of the *Z* and *E* diastereomers of **7**, obtained separately from the HBr addition products of methyl phenylpropiolate,[5] allowed the approach to preequilibrium (63 ± 4% *Z*, 290°, DPE) from both sides. The nature of the pyrolytic isomerization for **4–7** which accompanied fragmentation to methyl bromide was not established, and heterogeneous as well as molecular mechanisms are possible.[6]



$$R(X)C{=}CHCO_2Me \longrightarrow MeX + CO_2$$

4, R = CO_2Me; X = Cl
5, R = CO_2Me; X = Br
6, R = CO_2Me; X = I
7, R = Ph; X = Br



9

The "parent" system, methyl 3-bromopropionate (**8**), and **9** were also pyrolyzed. The conditions for production of methyl halide for these esters as well as for **1** and **4–7** are compiled in Table I. First-order rate constants, readily obtained from the spectral appearance of methyl halide vs. an internal standard on pyrolysis in sealed NMR tubes, represent rates of decomposition at low conversion only. The kinetics were generally complex with first-order plots showing upward curvature (autocatalysis, vide infra). The low conversion rate data showed some scatter, but were considered valuable in revealing major structure–reactivity relationships. (1) An "element" effect (X = Cl vs. Br vs. I) results in relative rates of approximately 1:10:50 for decomposition of **4–6**, respectively (DPE, 290°). (2) Stereoisomers **1**, which do not interconvert under the pyrolysis conditions, show similar reactivities. (3) An increase in pyrolysis solvent polarity (DPE, ϵ_{20} = 3.7 vs. NB ϵ_{25} = 34.8) results in only a slight increase in initial rate (~ten times). A large rate acceleration is observed in dimethylformamide (DMF) (ϵ_{25} = 36.7), but this solvent effect may very well be specific (vide infra) rather than general (polar). (4) Comparison of **5** and **7** reveals little substituent effect, Ph vs. CO_2Me.

Radical scavengers, hydroquinone, stilbene, or oxygen (as well as DPM, Table I), inhibited the decomposition to methyl halide slightly at most and acetic acid or an increase in surface to volume ratio with the introduction of glass wool did not appreciably affect the rate. (See paragraph at end of paper regarding supplementary material.) Methyl propiolate, phenylacetylene, and 2-bromo-2-butene, expected products of debromocarbomethoxylative elimination of **4–7** and **9**, were found in no more than trace amounts in pyrolysis mixtures. Although these olefins were relatively stable at elevated temperatures, they were destroyed during copyrolysis with the halo esters.

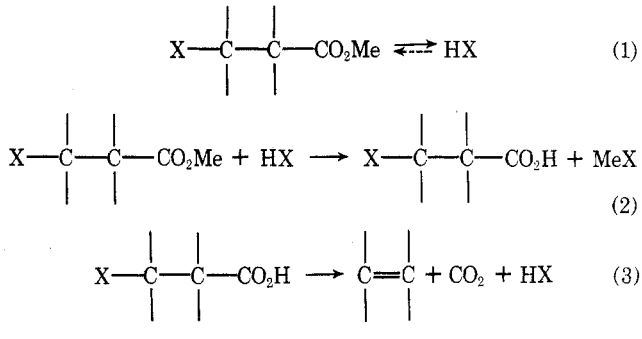
Several mechanisms for formation of MeX and putative elimination product from the halo esters have been considered. A pericyclic decomposition reminiscent of that proposed for halogenolytic rearrangement of bromoketals[7-9] is discounted since **5** or **6** did not give MeX in the gas phase (flow system, 5–10 sec contact time). Decomposition (500°) and geometrical isomerization (420°) were observed in these experiments, and MeX and methyl propiolate were shown to survive the pyrolysis conditions. An ion-pair mechanism for fragmentation is possible, but large solvent[10] and substituent effects[11] on the rate are expected but not observed. We find the mechanism of Scheme I

Table I
Methyl Halide Formation in the Pyrolysis of β-Halo Esters

Starting halo ester	Concn, *M*	Solvent	Pyrolysis temp, °C	*k*, sec^{-1} [a]
1 (cis)	0.8	DPM	240	1.3×10^{-4}
	0.5	NB	240	6.8×10^{-4}
	0.6	DPE	240	4.6×10^{-5}
	0.3	DPE	240	7.6×10^{-5}
1 (trans)	0.3	DPE	240	1.1×10^{-4}
4 (*E*)	1.2	DPE	290	1.6×10^{-6}
5 (*E*)	1.4	DPE	290	1.3×10^{-5}
	1.4	NB	290	1.8×10^{-4}
5 (*Z*)	0.7	DPE	290	1.2×10^{-5}
6 (*E*)	0.8	DPE	250	5.7×10^{-6}
	1.4	DPE	290	7.3×10^{-5}
	0.8	NB	250	1.9×10^{-5}
	1.4	DMF-d_7	160	7.3×10^{-6}
7 (*E* + *Z*)	1.1	DPE	290	5.2×10^{-5}
7 (*E*)	0.3	DPE	290	2.5×10^{-5}
	0.7	NB	290	4.4×10^{-4}
8	0.8	DPE	290	2.6×10^{-4}
	0.8	DMF-d_7	160	1.1×10^{-4}
9	0.8	DPE	210	9.4×10^{-5}
	1.0	NB	190	2.2×10^{-4}

[a] Pseudo-first-order appearance of methyl halide; generally three to six points at 10–30% conversion, ±30%.

Scheme I



more in accord with the experimental findings. It involves the production of HX in an initiation step, either via molecular (but less likely radical[12]) 1,2 elimination or perhaps by some more complicated route,[13] followed by halogenolytic displacement on starting ester (step 2).[14] The products of such 1,2 HX elimination were not generally detected, but consistent low yields of methyl acrylate were obtained on pyrolysis of **8**. Propagation of a chain elimination sequence results from debromocarboxylation of derived β-halo acid (step 3).[15]

An examination of rates reported for HX elimination[12] (possible step 1), halogenolysis[14] (step 2), and decarboxylative elimination[15] (step 3) suggests that the first of these processes should be initially rate determining (and should not display large polar substituent and solvent effects) followed by relatively rapid consumption (and regeneration) of HX. Application of the steady state assumption for the formation and destruction of HX and assuming the poor competitive position of k_{-1} leads to eq 4, which relates the rate of production of methyl halide to steps in Scheme I.

$$\frac{d(MeX)}{dt} = k_1 (\text{halo ester}) + k_3 (\text{halo acid}) \qquad (4)$$

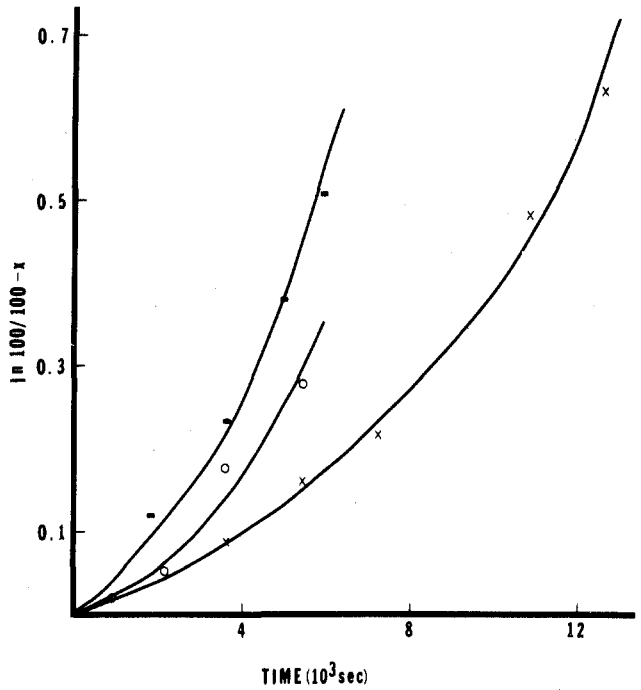


Figure 1. First-order plots for the appearance of methyl halide in the uncatalyzed pyrolysis of **1** (cis isomer, 0.6 *M* in DPE, 240°) (×), **5** (*E* isomer, 1.8 *M* in DPE, 290°) (○), and **6** (*E* isomer, 1.4 *M* in DPE, 290°) (■). X = % appearance of MeX.

Representative rate data, potentially testing the mechanism of Scheme I and eq 4, are shown graphically in Figure 1. The deviation from first-order behavior (autocatalysis) is apparent for halo esters **1**, **5**, and **6** (**4** and **7** behave similarly) and is consistent with early rate-determining HX elimination (initiation) (step 1, k_1) with rapidly increasing dependence on the rate of halo acid decomposition (propagation) (step 3, k_3) where $k_3 > k_1$.[16]

GLC identification of elimination and HX trapping product in variable low yield for one substrate provided direct evidence for the involvement of decarboxylative elimination in halo ester decomposition. Thus, in several experiments, pyrolysis of **7** (*Z* or *E*), 0.7 *M* in NB, at 290° gave phenylacetylene and α-bromostyrene in 9–17 and 4–27% yield, respectively. Elimination product instability, presumably owing to myriad destructive (polymerization) paths under the conditions employed, mitigated the reproducibility of such experiments as well as extension to the other substrates.

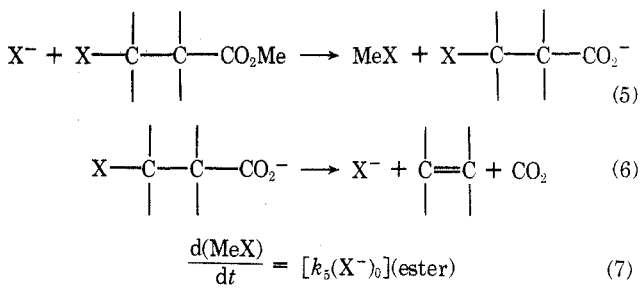
Other chain mechanisms for halo ester decomposition involving free radicals are possible but appear less likely. Halogen atoms produced from halo ester in an initiation step could bring about homolytic halogenolysis followed by radical decarboxylative elimination (regenerating halogen atom) equivalent to the mechanism of Scheme I. Objectionably, this path involves a free radical displacement on carbon (S H_2 reaction) which has been rarely observed, only where displacement is accompanied by the opening of a small ring.[17] Moreover, the aromatic solvents employed would have readily diverted halogen atoms for aromatic substitution.[18] Also, NB is an effective inhibitor of halogen atom chain reactions.[18b] A second possibility involving methyl radical as a chain carrier is similarly improbable.

Certain additives dramatically catalyzed the pyrolytic formation of methyl halide. For example, **1** (cis), **4** (*E*), **6** (*E*), and **9** with 10 mol % NaBr in DMF-d_7 or CD_3CN fragmented at a moderate rate at 160°. Decomposition was also brought about well below the normal pyrolysis temperatures with the introduction of LiBr, NaI, or HBr in DPE, NB, or CD_3CN. Pyridine and X_2 (with peroxide) were also catalysts, presumably by providing the effective ingredient, nucleophilic halogen, through base-catalyzed 1,2 elimination and radical hydrogen abstraction, respectively.[19]

That catalyzed halogenolysis was accompanied by decarboxylative elimination was confirmed in "crossover" and preparative (vide infra) experiments. For example, both MeBr and MeCl were obtained from **4** and 25 mol % HBr in DPE (165°) with MeBr predominating at low conversion. Similarly, **5** gave predominantly MeBr on pyrolysis in DPE at 165° with the addition of small amounts of iodine and benzoyl peroxide. MeBr and MeI were produced in roughly equal amounts when **6** was pyrolyzed at 250° with 100 mol % aqueous HBr in DPE. The time dependence of the methyl halide ratio was uncertain since the methyl halides in control experiments scrambled moderately. In DMF both starting halo esters and methyl halides[20] underwent exchange under "crossover" catalysis conditions. However, the halo esters were shown to be stable in DPE so that the observed crossovers remain significant, implicating the ionic chain eliminative decomposition. Finally, in view of the nature of the catalysis, the specific accelerating effect of DMF solvent (Table I) may be understood in terms of its known reaction with organic halides to give nucleophilic halogen.[21,22]

The probable course of catalyzed halogenolysis–elimination is shown in Scheme II. Halogenolysis of esters[14,23]

Scheme II



(even with decarboxylation)[24] is well known, and several examples of decarboxylative elimination of β-halocarboxylates[25] (including important relatives of **4**–**7**[15]) have appeared. If step 5 be rate limiting in the chain sequence or if halogenolysis and elimination be concerted (steps 5 and 6 combined), then (X^-) will remain unchanged, over the course of decomposition, justifying simplification to first order of the rate law for the formation of methyl halide (eq 7). A first-order plot (see supplementary material) for methyl halide appearance from **1** (catalyzed by NaBr in CD_3CN, 135°) is nonlinear. The steady state assumption concerning X^- in this case appears invalid; i.e., eliminative replenishment of X^- (step 6) lags consumptive halogenolysis (step 5). The production of MeX deviates from first order if second-order halogenolysis (presumably through the $B_{A1}2$ mechanism[23a]) is initially rate determining until *added* halogen is virtually consumed and the (slower) rate of decarboxylative elimination becomes important. That the overall decomposition is nonconcerted is supported by direct evidence. Aqueous extraction followed by acidification and work-up of a solution of **7** and 100 mol % NaBr in DMF-d_7 partially pyrolyzed at 145° yields an acidic fraction, whose ir spectrum is identical with that of a mixture of isomers of the parent acid of **7** and which can be esterified (CH_2N_2) for GLC comparison (38% yield), and an organic fraction containing CH_3Br, phenylacetylene (trace), and recovered **7** (48%).

Table II
Elimination Products from Catalyzed Dehalocarbomethoxylation of β-Halo Esters

Halo ester (concn, M)	Catalyst (10 mol %)[a]	Solvent	Pyrolysis temp, °C	Elimination product (% yield)[b]
1 (cis) (1.4)	NaBr	DMF	160	3 (25)
1 (trans) (1.0)	NaBr 18-Crown-6	CD_3CN	135	3 (30)
4 (*E*) (1.2)	NaI	DMF-d_7	160	Methyl propiolate (10)
5 (*E*) (1.2)	NaBr	DMF-d_7	160	Methyl propiolate (43)
6 (*E*) (1.4)	NaBr	DMF-d_7	160	Methyl propiolate (23)
	NaBr 18-Crown-6	CD_3CN	145	Methyl propiolate (52)
7 (*E*) (1.0)	NaBr 18-Crown-6	CD_3CN	155	Phenylacetylene (47)

[a] Mol % halo ester. [b] NMR and/or GLC analysis.

In summary, the evidence concerning pyrolytic fragmentation of β-halo esters (shown to be general with a variety of substrates) is consistent with a mechanism involving production in an initiation step of catalytic amounts of HX which subsequently leads to propagative halogenolysis–decarboxylation–elimination (Scheme I). This type of ionic chain elimination involving nucleophilic displacement by halogen appears to be without precedent, although a non-chain displacement-induced elimination has been reported.[26] These reactions are further examples of "fragmentation", the considerable generality of which has been demonstrated by Grob.[25a]

It is unlikely that *uncatalyzed* dehalocarbomethoxylation of β-halo esters will be of synthetic utility owing to the high temperatures involved. On the other hand, *catalyzed* fragmentation appears somewhat more promising. A limited survey of elimination yields is shown in Table II.[19] Catalysis in the presence of a crown ether, known to effectively promote displacement[27] and decarboxylation,[28] gave the best results. The latter conditions might well produce good yields where elimination products are not so readily polymerized. The utility of fragmentation may be confined to methyl esters owing to their ready displacement relative to other groups.[23a,24] In point of fact, ethyl 3-bromopropionate (in contrast to 8) gave ethyl acrylate in good yield at 290° in DPM but no ethyl bromide.

Experimental Section[19]

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer using chloroform as the solvent except as indicated. The NMR spectra were run using a JEOL (Japan Electronic Optical Laboratory Co. Ltd.) C-60 HL high-resolution spectrometer and carbon tetrachloride as the solvent except as indicated.

All preparative gas chromatography was performed using a Varian Aerograph 90-P instrument equipped with a thermal conductivity detector and helium as the carrier gas. Analytical VPC was performed either on a Varian Aerograph 90-P, 920 (thermal conductivity detector), or 1400 (flame ionization detector). Columns and conditions used for specific analyses are listed in Table III. Carrier gas flow rates were 60–80 ml/min.

Dimethyl 1,2-dibromo-1,2-cyclobutanedicarboxylate (1) (cis and trans),[3] methyl β-bromocinnamate (7) (*E* and *Z*),[5] and methyl 2,3-dibromo-2-methylbutanoate (9) (threo)[29] were prepared as reported and ethyl and methyl 3-bromopropanoate (8) were obtained commercially. Pyrolysis solvents diphenylmethane (DPM), diphenyl ether (DPE), nitrobenzene (NB), and dimethylformamide (DMF) were distilled from sodium carbonate. Sodium bromide and iodide and lithium bromide were commercial samples used as received.

Methyl 2-Bromo-1-cyclobutene-1-carboxylate (2). Titration of an ether solution of 2-bromocyclobutene-1-carboxylic acid (mp 121–122°, lit.[15b] mp 121–122°), prepared from 1,2-dibromo-1,2-cyclobutanedicarboxylic acid,[15b] with a solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea[30] gave after routine work-up methyl 2-bromo-1-cyclobutene-1-carboxylate (2) as an oil which could be purified by GLC (column D). The spectral data follow: ir 5.75 μ; NMR δ 2.75 (s, 4 H, $-CH_2-$), 3.80 (s, 3 H, $-CO_2CH_3$).

Anal. Calcd for $C_6H_7BrO_2$: C, 37.85; H, 3.69; Br, 41.70. Found: C, 37.89; H, 3.88; Br, 41.80.

Methyl 3-Bromo-1,3-butadiene-2-carboxylate (3). GLC injector port (250°) pyrolysis of methyl 2-bromo-1-cyclobutene-1-carboxylate (2) (column D, 170°) gave (separate from recovered cyclobutene) an oil which polymerized on standing as a neat sample. The material was stable, however, when collected as a solution in carbon tetrachloride, and was assigned the structure 3 on the basis of the spectral data: ir (CCl_4) 5.75 μ; NMR δ 3.80 (s, 3 H, $-CO_2CH_3$), 6.18 (m, 4 H, $-CH_2$). Tandem GLC–mass spectrometry revealed a parent ion at *m/e* 191 consistent with the formula $C_6H_7BrO_2$.

Dimethyl Chloromaleate (4). A solution containing chloromaleic anhydride (10.0 g, 0.076 mol), concentrated sulfuric acid (2 ml), and methanol (50 ml) was refluxed for 40 hr. The methanol was removed at reduced pressure and the residue neutralized with 10% sodium bicarbonate solution (20 ml) and extracted with two 20-ml portions of anhydrous ether. After drying ($MgSO_4$) the ether was removed in vacuo. The crude yellow oil which remained was distilled, giving 12.0 g (89%) of dimethyl chloromaleate, bp 52–53° (0.25 mm), lit.[4] bp 100° (17.0 mm). The product was further purified by preparative GLC (column D): NMR δ 3.48 (s, 3 H, $-CO_2CH_3$), 3.55 (s, 3 H, $-CO_2CH_3$), 6.40 (s, 1 H, –CH).

Dimethyl Bromomaleate (5).[4] A solution containing bromomaleic anhydride (10.0 g, 0.057 mol), concentrated sulfuric acid (2 ml), and methanol (50 ml) was refluxed for 40 hr. The methanol was removed at reduced pressure and the residue neutralized with 10% sodium bicarbonate solution (20 ml) and extracted with two 20-ml portions of anhydrous ether; the ether was then removed at reduced pressure, giving 11.18 g of crude dimethyl bromomaleate, which was purified by preparative GLC (column D). The NMR spectrum displayed signals at δ 3.72 (s, 3 H, $-CO_2CH_3$), 3.85 (s, 3 H, $-CO_2CH_3$), 6.45 (s, 1 H, –CH).

Dimethyl Iodomaleate (6). A solution containing bromomaleic anhydride (5.0 g, 0.028 mol), sodium iodide (4.2 g, 0.028 mol), and acetone (20 ml)[31] was refluxed for 13 hr. This solution was filtered while still hot and the acetone removed at reduced pressure, giving 5.1 g (81%) of iodomaleic anhydride. A solution of the crude anhydride, sulfuric acid (1 ml), and methanol (30 ml) was refluxed for 40 hr. The methanol was removed at reduced pressure and the residue neutralized with 10% sodium carbonate solution (20 ml) and extracted with two 20-ml portions of anhydrous ether. The crude

Table III

Column[a]	Substrate	Oven temp, °C
A, 10 ft × 0.25 in. 20% GE SF-96	1	160–200
	4–6	100–160
	7	180
	9	90–95
B, 10 ft × 0.375 in. 20% GE SF-96	1	160
C, 10 ft × 0.25 in. 20% Carbowax	1, 3	135–170
D, 10 ft × 0.375 in. 20% FFAP	2, 4–6	100–160

[a] Stationary support, 60/80 mesh Chromosorb W.

product from the ether layer was recrystallized from ethanol giving 4.2 g (71%) of dimethyl iodomaleate, mp 59–60°. The spectral data follow: NMR δ 3.75 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, CO_2CH_3), 6.6 (s, 1 H, –CH); ir 5.80 and 6.20 μ.

Anal. Calcd for $C_6H_7IO_4$: C, 26.7; H, 2.59. Found: C, 27.42; H, 2.99.

Pyrolysis Apparatus and Procedures. Static pyrolysis was carried out in evacuated sealed medium wall NMR tubes. The procedure for preparation of the pyrolysis tubes included the following: washing with chromic acid cleaning solution; rinsing with distilled water, ammonium hydroxide, distilled water, and acetone; drying at 100° for 1 hr. The tubes were filled by syringe from stock solutions, evacuated through one freeze–thaw cycle, and sealed.

The apparatus for static pyrolysis at temperatures less than 160° consisted of a 6-l. stainless steel beaker equipped with a 3-ft coiled 500-W immersion heater. Power to the heater was provided by line voltage regulated with a powerstat transformer and an I^2R L7/600 Therm-O-Watch. The bath fluid was General Electric SF-96. Stirring was effected by a Lightnin' constant speed heavy duty stirrer regulated by a powerstat transformer for variable speed, and temperature was maintained within ±1.0°. For temperatures of 160° or greater a 6-l. stainless steel beaker equipped with a 3-ft coiled 500-W immersion heater and a 500-W knife blade heater was used. The immersion heater was powered as above; the knife blade was powered by an I^2R L7/600 Therm-O-Watch. The bath fluid was a molten mixture of potassium nitrate and sodium nitrite (1:1 w/w). Efficient stirring was provided by a transformer for variable speed. Insulation for the system was provided by a layer (2–4 in.) of vermiculite surrounding the beaker. The apparatus was contained in a 5-gal metal cylinder. The temperature fluctuation was maintained at ±0.5°. Mixtures to be pyrolyzed contained in NMR tubes prepared as described above were held in the bath by a stainless steel cylindrical tube holder and on removal from the pyrolysis bath were quenched in a beaker of water maintained at room temperature.

Product Analysis. Kinetics. Pyrolyses were interrupted intermittently and tubes analyzed directly by NMR for the appearance of methyl halide in the δ 2–3 region vs. an internal standard, *tert*-butylbenzene or DPM (methylene protons). Use of the integrated first-order rate equation gave rate constants for methyl halide appearance at low conversion (10–30%). The fragmentation to methyl halide for **4**–**7** was accompanied by the appearance of new olefinic and –OMe signals assignable to the geometric isomers of starting halo esters. Thus, for example, to the pattern of resonances in NB for dimethyl bromomaleate (**5**) at δ 3.40, 3.55, and 6.10 were added absorptions at δ 3.48, 3.55, and 7.03, which were associated with dimethyl bromofumarate[4] isolated from a partial pyrolysate (ir 5.8 μ). Pyrolysates were further examined by GLC for the appearance of methyl propiolate, phenylacetylene, and 2-bromo-2-butene (cis and trans) with authentic samples for comparison using coinjective techniques.

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Registry No.—*cis*-**1**, 10359-27-0; *trans*-**1**, 10358-76-6; **2**, 57325-23-2; **3**, 57325-24-3; **4**, 19393-45-4; (*E*)-**5**, 20688-29-3; (*Z*)-**5**, 2509-16-2; **6**, 57325-25-4; (*E*)-**7**, 1884-33-9; (*Z*)-**7**, 1884-32-8; **8**, 3395-91-3; **9**, 28127-71-1; 2-bromocyclobutene-1-carboxylic acid, 57325-26-5; diazomethane, 334-88-3; chloromaleic anhydride, 96-02-6; methanol, 67-56-1; bromomaleic anhydride, 5926-51-2; sodium iodide, 7681-82-5.

Supplementary Material Available. Tables of rate data for pyrolyses in the presence of additives (catalysts) along with kinetics plots for catalyzed and uncatalyzed fragmentation (4 pages) will appear following these pages in the microfilm edition of this volume of the journal.

References and Notes

(1) A portion of this work was presented at the 5th Northeast Regional Meeting of the American Chemical Society, Rochester, N.Y., 1973, Abstract No. 263.
(2) G. Jones, II, and M. E. Fantina, *J. Chem. Soc., Chem. Commun.*, 375 (1973).
(3) E. Lustig, E. P. Ragelis, N. Duy, and J. A. Ferretti, *J. Am. Chem. Soc.*, **89**, 3953 (1967).
(4) K. von Auwers and L. Haues, *Ber.*, **62B**, 1678 (1929).
(5) K. Bowden and M. J. Price, *J. Chem. Soc. B*, 1472 (1970).
(6) (a) H.-O. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1972); (b) H. Steinmetz and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 4141 (1952); (c) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).
(7) J. E. Baldwin and J. E. Gano, *Tetrahedron Lett.*, 1101 (1969).
(8) For evidence against such a concerted fragmentation, see J. Salaun, B. Garnier, and J. M. Conia, *Tetrahedron*, **29**, 2895 (1973).
(9) For a series of perhaps related fragmentations, see L. A. Paquette and R. W. Houser, *J. Am. Chem. Soc.*, **93**, 944 (1971), and references cited therein.
(10) H. Kwart and M. T. Waroblak, *J. Am. Chem. Soc.*, **89**, 7145 (1967).
(11) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *J. Am. Chem. Soc.*, **96**, 1100 (1974), and references cited therein.
(12) (a) G. G. Smith and F. W. Kelly, *Prog. Phys. Org. Chem.*, **8**, 75 (1971); (b) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).
(13) For example, dibromides **1** and **9** might initiate decomposition by elimination of Br_2 which dissociates giving HBr after hydrogen abstraction.
(14) (a) R. K. Solly and S. W. Benson, *J. Phys. Chem.*, **74**, 4071 (1970); (b) Y. Sakaguchij, T. Ono, and T. Ueda, *Kobunski Kagaku*, **22**, 696 (1965).
(15) (a) C. A. Grob, J. Csapilla, and G. Cseh, *Helv. Chim. Acta*, **47**, 1590 (1964); (b) W. H. Perkin, *J. Chem. Soc.*, 950 (1894).
(16) Decomposition of **8** and **9** was strictly first order (see supplementary material). Decarboxylative elimination products were not identified for these systems. Since kinetic support for Scheme I (autocatalysis) was not obtained, a mechanism not to be ruled out for decomposition is HX formation followed by indiscriminate attack on any ester group (starting material or product) which leads to methyl halide but not necessarily to dehalocarbomethoxylation.
(17) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N.Y., 1971, p 72.
(18) (a) M. L. Poutsma in "Methods in Free Radical Chemistry", Vol. I, E. S. Huyser, Ed., Marcel Dekker, New York, N.Y., 1969, p 79; (b) B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957).
(19) For more details, see M. E. Fantina, Dissertation, Boston University, 1976.
(20) (a) A. J. Parker, *J. Chem. Soc.*, 4398 (1961); (b) A. J. Parker, *Aust. J. Chem.*, **16**, 585 (1963).
(21) (a) M. Anteunis and H. L. Peeters, *J. Org. Chem.*, **40**, 307 (1975); (b) W. K. Kwok and S. I. Miller, *J. Org. Chem.*, **35**, 4034 (1970); (c) J. L. Neumeyer and J. G. Cannon, *ibid.*, **26**, 4681 (1961); (d) N. Kornblum and R. K. Blackwood, *J. Am. Chem. Soc.*, **78**, 4037 (1956).
(22) The methyl halide products as well as starting halo esters appeared to be reacting with DMF. Their production, instead of accelerating at high conversion, fell off in this solvent in uncatalyzed pyrolyses.
(23) (a) P. Muller and B. Siegfried, *Helv. Chim. Acta*, **57**, 987 (1974); (b) N. J. Daly and M. F. Gilligan, *Aust. J. Chem.*, **24**, 1823 (1971); (c) D. Klamann, *Monatsh. Chem.*, **83**, 1398 (1952); (d) F. Eisinger, J. Schreiber, and A. Schenmoser, *Helv. Chim. Acta*, **43**, 113 (1960); (e) P. D. C. Dean, *J. Chem. Soc.*, 6655 (1965).
(24) For a set of observations interestingly similar to our own, but concerning a different system, see J. J. Wilczynski and H. W. Johnson, Jr., *J. Org. Chem.*, **39**, 1909 (1974). For other halogenolysis–decarboxylations, see A. P. Krapcho, E. G. E. Jahngen, Jr., and A. J. Lovey, *Tetrahedron Lett.*, 1091 (1974); C. L. Liotta and F. L. Cook, *ibid.*, 1095 (1974); D. J. Cram et al., *J. Am. Chem. Soc.*, **95**, 4210, 4237 (1973); P. Muller and B. Siegfried, *Tetrahedron Lett.*, 3565 (1973); B. M. Trost and T. J. Dietsche, *J. Am. Chem. Soc.*, **95**, 8200 (1973); K. Blaha and J. Rudinger, *Collect. Czech. Chem. Commun.*, **30**, 585 (1965).
(25) (a) C. A. Grob and P. W. Schless, *Angew. Chem., Int. Ed. Engl.*, **6**, 1 (1967); (b) E. R. Trumbull, R. T. Finn, K. M. Ibne-Rasa, and C. K. Sauers, *J. Org. Chem.*, **27**, 2339 (1962).
(26) E. S. Behare and R. B. Miller, *Chem. Commun.*, 402 (1970).
(27) F. L. Cook, C. W. Bowers, and C. L. Liotta, *J. Org. Chem.*, **39**, 3416 (1974), and references cited therein.
(28) D. H. Hunter, W. Lee, and S. K. Sim, *J. Chem. Soc., Chem. Commun.*, 1018 (1974).
(29) R. E. Buckles and G. V. Mock, *J. Org. Chem.*, **15**, 680 (1950).
(30) N. Rabjohn, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 250.
(31) T. Cohen and T. Poeth, *J. Am. Chem. Soc.*, **94**, 4363 (1972).
(32) NOTE ADDED IN PROOF. Since the submission of our manuscript, results similar to our own involving catalyzed dehalocarbomethoxylation of β-halo esters have been reported; see P. Ykman and H. Kǐ Hall, Jr., *Tetrahedron Lett.*, 2429 (1975).