Addition of Halogens to Vinylcyclopropanes

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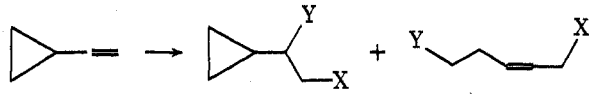
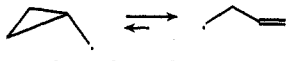
The halogenation of vinylcyclopropane (1) and 2-cyclopropylpropene (4) with chlorine, bromine, methyl hypochlorite (CH_3OCl), iodobenzene dichloride (IBD), and trichloroamine (NCl_3) is reported. A comparison of the product distribution from these halogenating reagents with 1 and 4 under ionic and radical conditions is used to distinguish between radical or cationic intermediates in these reactions. Chlorine, bromine, and NCl_3 react with 4 by an ionic process while IBD reacts primarily by a radical process. When 4 is treated with CH_3OCl the reaction proceeds by an ionic or radical mechanism depending on the reaction conditions. Apparently these reagents tend to react with vinylcyclopropanes by an ionic process because a very stable cyclopropylcarbinyl cation intermediate can be formed.

The addition of electrophiles[1] and radical addends[2] to vinylcyclopropanes is an area of current interest. It has been demonstrated that reactions which proceed through cyclopropylcarbinyl cation intermediates[1f] give predominantly cyclopropyl products under conditions of kinetic control.[1c,3]



When product formation is reversible, equilibration leads to formation of the thermodynamically more stable homoallyl isomer owing to relief of strain energy in the cyclopropane ring.[1c] Radical additions to vinylcyclopropanes proceed through classical cyclopropylcarbinyl and homoallyl intermediates.[2,4] Since at equilibrium the homoallyl radical is favored over the cyclopropylcarbinyl radical,[2c,4] a decrease in

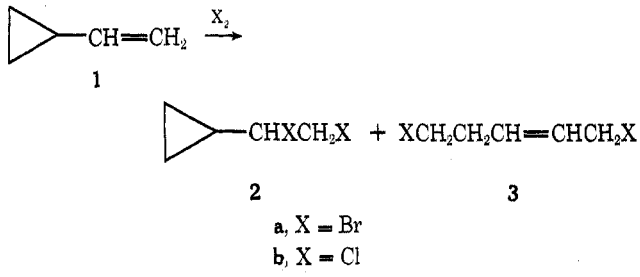


the concentration of the radical chain transfer agent will cause an increase in the amount of ring-opened products. These criteria have been used to confirm the presence of radical intermediates in the cyclopropylcarbinyl system.[2b]

In this study we investigated the halogenations of vinylcyclopropane (1) and 2-cyclopropylpropene (4) with chlorine, bromine, methyl hypochlorite, iodobenzene dichloride (IBD), and trichloroamine (NCl_3). It seemed to us that a comparison of the product distribution from the reaction of these halogenating reagents with 1 and 4 under various conditions would provide information about the intermediates in these reactions. A survey of the literature reveals that halogenation of vinylcyclopropanes has not been investigated thoroughly; only a product[1f] and kinetic[1a] study have appeared for the bromination of 1 under ionic conditions. The chlorinations of 1 and 4 have not been reported. Chlorine,[5] bromine,[5] and iodobenzene dichloride[6] are known to react by an ionic or radical process under the appropriate reaction conditions. Alkyl hypochlorites react with olefins by an ionic process in protic solvents.[7] The literature contains no unequivocal evidence for an ionic addition of alkyl hypochlorites to olefins in aprotic solvents.[7b,8] A radical process is involved when trichloroamine is treated with olefins[9a] and dienes.[9b] There is one reported case of an ionic process participating in the reaction of NCl_3 with olefins[9a] when a stable cation is formed.

Results and Discussion

In 1952 Slobodin[1e] reported that bromination of vinylcyclopropane 1 gave products **2a** and **3a** in a ratio of 3:2, respectively. During our investigation of the halogenations of vinycyclopropanes we found the product ratio for the bromination of 1 to be 6:1 by NMR analysis (Table I).[10,11] When 1 was treated with chlorine a similar ratio of products was observed.[12] This large preference for the 1,2 products is consistent with a cyclopropylcarbinyl cation[1c,3] intermediate and is in agreement with the open-cation intermediate proposed by Tidwell and Yates[1a] for the bromination of 1.



a, X = Br
b, X = Cl

Bromination of 4 gives 1,2 and 1,5 products, while the chlorination of 4 gives substitution and 1,2 products but no 1,5 products.[13] The substitution products, 8 and 9, in the chlorination of 4 are also consistent with an ionic but not a radical mechanism since formation of these products via a radical intermediate would involve transfer of a hydrogen atom. It appears that product 10 is formed by addition of HCl to 4 since direct treatment of 4 with HCl under the reaction conditions resulted in rapid formation of 10.

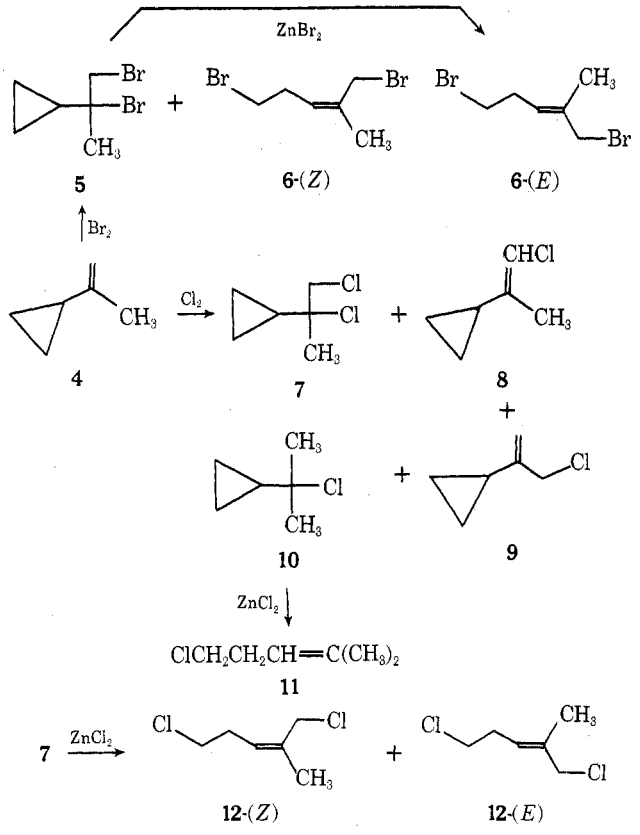


Table I. Halogenation of Vinylcyclopropanes 1 and 4

Run	Solvent	Mole fraction 1 or 4	Reaction[a] conditions	Halogenating reagent[b]	Percent products[c] From 1 2	From 1 3	From 4 5 or 7	From 4 6 or 12	From 4 8	From 4 9	From 4 10
1	C_5H_{12}	0.020	O_2, dark	Br_2	91	9	84	16			
2	CCl_4	0.020	O_2, dark	Br_2	86	14	83	17			
3	CH_2Cl_2	0.020	O_2, dark	Br_2	89	11	83	17			
4	Ether	0.094[d]		Br_2	86	14					
5	CCl_4	0.020	N_2, uv	Br_2			85	15			
6	CCl_4	0.500	N_2, uv	Cl_2			34		16	28	22
7	C_5H_{12}	0.020	O_2, dark	Cl_2	91[e]	9	33		14	47	6
8	CCl_4	0.020	O_2, dark	Cl_2			33		13	38	16
9	CH_2Cl_2	0.020	O_2, dark	Cl_2	90[e]	10	32		19	21	28
10	CH_2Cl_2	0.006[f]	O_2, dark	IBD			44	32	9	7	8
11	CH_2Cl_2	0.035[f]	N_2, uv	IBD			52	48			
12	CH_2Cl_2	0.012[f]	N_2, uv	IBD			43	57			
13	CH_2Cl_2	0.006[f]	N_2, uv	IBD			34	66			
14	CH_2Cl_2	0.003[f]	N_2, uv	IBD			28	72			
15	CH_2Cl_2	1.5×10^{-3} [f]	N_2, uv	IBD			24	76			
16	CH_2Cl_2	7.5×10^{-4} [f]	N_2, uv	IBD			20	80			
17	CH_2Cl_2	0.020	O_2, dark	NCl_3			52		20	28	
18	CCl_4	0.020	O_2, dark	NCl_3			50		18	32	
19	CCl_4	0.050	N_2, uv	NCl_3			50		22	28	
20		Neat	N_2, uv	NCl_3			46		20	34	

[a] The uv light was from a 275-W General Electric sunlamp. [b] Vinylcyclopropanes 1 and 4 were used in excess (ca. 10–40%). Neat bromine was added to the reaction mixture at −15 °C. A slow stream of N_2 or O_2 was used as a carrier gas to transport Cl_2 into the reaction mixture at −15 °C. A 6.0 M solution of 4 in CH_2Cl_2 was added to IBD dissolved in CH_2Cl_2 at 25 °C. NCl_3 was added dropwise as a 0.34 M solution in CCl_4 or CH_2Cl_2. [c] Product composition was determined by NMR analysis on an average of at least three runs. [d] Conditions under which Slobodin carried out the bromination of 1; see ref 1e. [e] Similar ratios were obtained by VPC. See ref 20. [f] Mole fraction IBD in CH_2Cl_2.

The data in Table I show that when 4 is treated with chlorine under ionic conditions (low mole fraction olefin, O_2 as an inhibitor, dark) or radical conditions (high mole fraction olefin, O_2 removed by N_2, and ultraviolet illumination) there is little change in the product distribution. This suggests that a radical intermediate is not involved in the chlorination of vinylcyclopropanes. Apparently the radical pathway does not compete effectively when chlorine is treated with vinylcyclopropanes because a very stable cyclopropylcarbinyl cation intermediate is formed.

Therefore, we turned our attention to halogenating reagents that might be more likely to react with vinylcyclopropanes by a radical mechanism. When 4 is treated with methyl hypochlorite under ionic conditions, in methylene chloride, products **7**, **8**, **9**, and **13** are formed in a slow reaction. This appears to be the first reported case of an ionic process for the reaction of methyl hypochlorite with olefins in an aprotic solvent. Apparently the ionic process is competitive because a very stable cyclopropylcarbinyl cation intermediate can be formed. However, when the reaction is carried out under radical conditions a fast reaction gives only anti-Markownikoff products

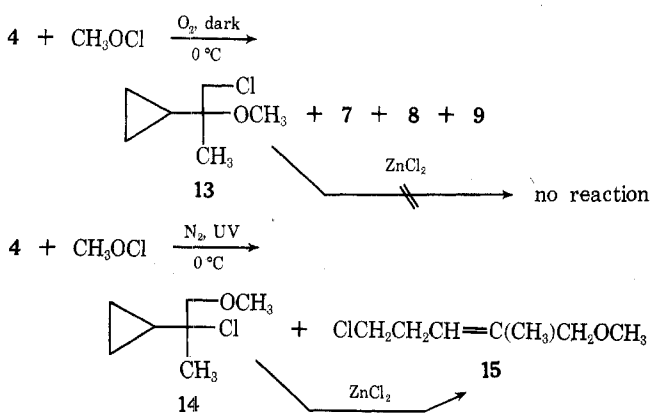


Table II. Reaction[a] of Methyl Hypochlorite with Vinylcyclopropane 4 under Radical Conditions at 0 °C

Mole fraction in CH_2Cl_2		Product composition	
CH_3OCl[b]	4	14	15
0.08	Neat	100	
0.03	0.2	85	15
0.03	0.1	80	20
0.03	0.02	66	34
0.03	0.002	58	42

[a] Yields are 60–75% obtained by NMR integration using benzene as an internal standard. [b] The methyl hypochlorite in methylene chloride was added dropwise to the olefin under nitrogen and ultraviolet illumination.

14 and **15**. Further support for a radical intermediate is obtained from the following dilution experiment. As the concentration of the olefin is decreased, the amount of 1,5 product is increased (Table II). These results show that there is an equilibrium of the cyclopropylcarbinyl and homoallyl intermediates which is consistent only with a radical process.

The chlorination of 4 with iodobenzene dichloride (IBD) gave primarily products **7** and **12** from a molecule induced homolysis reaction. A radical process was confirmed by a dilution experiment (Table I, runs 11–16). We were unable to inhibit the radical pathway completely using oxygen as the inhibitor as indicated by the large amount of 1,5 product **12** when 4 was treated with IBD under ionic conditions (Table I, run 10).[14]

When 4 is treated with trichloroamine, products **7**, **8**, and **9** are apparently formed by an ionic rather than a radical mechanism (Table I, runs 17–20). Formation of **8** and **9** is not consistent with a radical process since it would involve loss of a hydrogen atom from a radical intermediate. Apparently

products **8** and **9** are formed by loss of a proton from a cyclopropylcarbinyl cation intermediate to generate hydrogen chloride. Additional support for an ionic process comes from the absence of the 1,5 product (**12**), the insignificant change in product distribution as the concentration of the reagents is decreased (runs 19 and 20), and from the similar product distributions for the addition of chlorine and NCl_3 to **4**. In the case of NCl_3, product **10** is probably not formed because the hydrogen chloride, which is generated during the reaction, reacts with NCl_3 to form ammonium chloride.[15] We assume that the reaction of NCl_3 with **4** proceeds by an ionic mechanism because a very stable cyclopropylcarbinyl cation intermediate can be formed. This agrees with Kovacic's observation[9a] of a large ionic component for the reaction of NCl_3 with olefins such as isobutylene and norbornene which are also able to form stable cation intermediates.

Experimental Section

General. Vinylcyclopropane (**1**) was prepared by the pyrolysis of 1-cyclopropylethyl *S*-methyl xanthate as reported by Overberger.[16] 2-Cyclopropylpropene (**4**) was prepared by dehydration of dimethylcyclopropylcarbinol over sulfuric acid.[17] All other reagents and solvents were obtained commercially. Neat bromine was added from a small capillary dropper to magnetically stirred solutions. Chlorine was condensed in a calibrated capillary tube, and then allowed to distill into a stream of carrier gas (N_2 or O_2) which was bubbled into the reaction mixture. The initial reaction mixture contained an excess (10–40%) of **1** or **4**. Control experiments show that the 1,2 products are stable under the reaction conditions. Removal of the solvent and excess olefin was carried out on a rotary evaporator at room temperature and the product composition was determined by NMR analysis. The yields were determined by adding 30 μl of a 1.0 M solution of benzene, toluene, or 1,2-dichloroethane in CCl_4 as an internal standard to the crude products dissolved in ca. 300 μl of CCl_4. Nuclear magnetic resonance spectra were obtained on a Varian T-60A spectrometer and the infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. The VPC analysis was accomplished on a Hewlett-Packard 5750 flame ionization chromatograph. Collection of products by VPC was accomplished on an F and M 700 chromatograph. The following columns were used: column A, 6 ft × 0.25 in. stainless steel column of 5% SE-30 on 60/80 Chromosorb W; Column B, 12 ft × 0.25 in. 10% Carbowax 20M on Chromosorb W.

Reaction of Bromine with 1. To 38 mg (0.56 mmol) of **1** in a weighed amount of solvent (Table I) at −15 °C was added ca. 25 μl of neat bromine. The solvent was removed at room temperature on a rotary evaporator and an NMR spectra recorded to obtain the yield (100%) and product ratios (Table I). These NMR solutions were found to be stable at room temperature for several days. Several analytical runs were combined and short-path distillation gave **2a**, bp 45–47 °C (0.75 mm), with the following spectral properties: ir (CCl_4) 3090 (c-C_3H_5), 2940 (C–H), 1440 (C–H), 1130, 1015 (c-C_3H_5), 925 cm^{-1}; NMR (CCl_4) δ 0.30–1.0 (m, 4 H), 1.07 (m, 1 H), 3.6–4.0 (m, 3 H). The 1,5 product (**3a**) was not obtained free of **2a** by distillation. When **2a** was analyzed by VPC a mixture, ca. 50:50, of **2a** and **3a** was obtained.[10] The retention times for **2a** and **3a** were 14 and 25 min, respectively, on column A at 75 °C.

Isomerization of 2a to 3a. To a 70-mg (0.31 mmol) mixture of **2a** and **3a** (8:1, respectively) in 0.3 ml of reagent acetone at room temperature was added 15 mg of $ZnBr_2$.[12] After 2 h the reaction mixture was poured into 1.0 ml of water, extracted with three portions of methylene chloride, and dried over $MgSO_4$. The solvent was removed at reduced pressure, and a bulb-to-bulb distillation of the clear oil at 0.5 mm with an oil bath maintained at 60 °C gave 50 mg (72%) of a clear oil with the same VPC retention time as reported above for **3a** on column A. The following spectra were obtained: ir (CCl_4) 3030, 2970, 1670, and 1430 (C–H), 1255, 1200, 965 (C–H), 930 cm^{-1}; NMR (CCl_4) δ 2.63 (m, 2 H), 3.38 (t, J = 6.8 Hz, 2 H), 3.86 (m, 2 H), 5.78 (m, 2 H).

Reaction of Bromine with 4. The bromination was carried out on ca. 60-mg samples as described above. The yield (90%) and the product ratios were determined by NMR. A preparative reaction was carried out by adding 8.6 g (0.054 mol) of bromine dropwise to 4.92 g (0.06 mol) of **4** in 125 ml of pentane. The reaction mixture was maintained at −15 °C in an isopropyl alcohol bath by adding dry ice to the alcohol bath as needed. The solvent was removed on a rotary evaporator, and distillation[18] gave **5** (bp 41.0–41.5 °C, 0.5 mm) with the following spectral properties: ir (neat) 3090 (c-C_3H_5), 3000 (C–H), 1440 and 1370 (C–H), 1230, 1120, 1065, 1020 (c-C_3H_5), 895, 620, 590, and 565 cm^{-1} (C–Br); NMR (CCl_4) δ 0.30–0.85 (m, 4 H), 1.20 (m, 1 H), 1.75 (s, 3 H), 3.94 (s, 2 H).

Isomerization of 5. To 3.63 g (0.015 mol) of **5** in 15 ml of acetone was added 50 mg of $ZnBr_2$.[12] The reaction mixture was stirred at room temperature for 30 min at which time it was poured into 50 ml of water. The products were isolated as described above for **3a**. An NMR spectra of the crude oil showed that the products **6**-(*Z*) and **6**-(*E*) were formed in a 3:7 ratio, respectively.[19] Distillation gave 3.00 g (82%) of a mixture of **6**-(*Z*) and **6**-(*E*) (bp 64–67 °C, 0.65 mm) with the following properties: ir (neat) 3010 (C–H), 2960 (C–H), 1660 (C=C), 1445 (C–H), 1270, 1205, 750 (C–H), 610 cm^{-1}; NMR (CCl_4) δ 1.80 and 1.87 (two quartets, J = 0.6 and 1.1 Hz, respectively, 3 H), 2.62 (q, J = 6.6 Hz, 2 H), 3.34 (t, J = 6.6 Hz, 2 H), 3.90 (br s, 2 H), 5.55 (m, 1 H).

Chlorination of Vinylcyclopropane 1. The reactions were carried out at −15 °C in the dark in a solution which was 0.02 mole fraction in **1** (60–70 mg). Chlorine (20 μl) was distilled into a stream of oxygen and was bubbled into the reaction mixture. Analysis by VPC on column A at 55 °C gave products **2b** and **3b** with retention times of 8.0 and 16 min, respectively.[20] Analysis of the crude mixture by NMR showed that the products were formed in 40% yield and that the product ratios were similar to those obtained by VPC (Table I). The products were obtained pure by VPC collection on column A, and the following spectral properties were recorded: **2b**, ir (CCl_4) 3090 (c-C_3H_5), 2960 (C–H), 1440 (C–H), 1180, 1050, 1020 (c-C_3H_5), 950, 920, 900 cm^{-1}; NMR (CCl_4) δ 0.30–0.90 (m, 4 H), 0.95–1.3 (m, 1 H), 3.2–3.9 (m, 3 H); **3b**, ir (CCl_4) 3010 (C–H), 2960 (C–H), 1630 (C=C), 1440 (C–H), 1250, 970 cm^{-1} (C–H); NMR (CCl_4) δ 2.57 (m, 2 H), 3.52 (t, J = 6.8 Hz, 2 H), 4.00 (m, 2 H), 5.77 (m, 2 H).

Isomerization of 2b. To a 25-mg (0.18 mmol) mixture of **2b** and **3b** (8:1, respectively) in 0.3 ml of reagent acetone was added 15 mg of $ZnCl_2$.[12] After 1.5 h the products were isolated as described above for the isomerization of **2a**. Bulb-to-bulb distillation of the product at 10.0 mm with an oil bath maintained at 60 °C gave 20 mg of a clear oil with the same VPC retention time and spectra as reported above for **3b**.

Reaction of Chlorine with 4. A. Ionic Conditions. The chlorination was carried out on ca. 60 mg (0.02 mole fraction) of **4** as described above for the chlorination of **1**. The yields (32%) and product ratios were determined by NMR. Several of the analytical runs were combined and the products collected by preparative VPC. Product **7** was collect on column A and had a retention time of 9.0 min at 42 °C. The 1,2-dichloride **7** had the following spectral properties: ir (neat) 3090 (c-C_3H_5), 2980 (C–H), 1450 (C–H), 1430, 1370 (C–H), 1135, 1080, 1020 (c-C_3H_5), 905, 825, 785, 705 cm^{-1}; NMR (CCl_4) δ 0.35–0.70 (m, 4 H), 1.22 (m, 1 H), 1.59 (s, 3 H), 3.74 (s, 2 H). Products **8**, **9**, and **10** had retention times of 11, 15, and 9 min, respectively, on column B at 62 °C and gave the following spectral properties: **8**, ir (CCl_4) 3085 (c-C_3H_5), 3010 (C–H), 2930 (C–H), 1640 (C=C), 1440 and 1370 (C–H), 1205, 1075, 1020 (c-C_3H_5), 925, 905, 815 cm^{-1}; NMR (CCl_4) δ 0.35–0.70 (m, 4 H), 1.30 (m, 1 H), 1.63 (d, J = 1.3 Hz, 3 H), 5.78 (p, J = 1.3 Hz, 1 H); **9**, ir (CCl_4) 3085 (c-C_3H_5) 3010 (C–H), 2970 (C–H), 1640 (C=C), 1445 (C–H), 1425 (C–H), 1260, 1020 (c-C_3H_5), 905 (C–H), 710 cm^{-1}; NMR (CCl_4) δ 0.40–0.83 (m, 4 H), 1.22 (m, 1 H), 4.02 (d, J = 0.9 Hz, 2 H), 4.79 (m, 1 H), 5.00 (dd, J = 1.7 and 0.9 Hz, 1 H); **10**, ir (neat) 3085 (c-C_3H_5), 2960 (C–H), 1450 and 1360 (C–H), 1290, 1260, 1230, 1150, 1113, 1020 (c-C_3H_5), 995, 885, 780, 655, and 595 cm^{-1}, in reasonable agreement with the Raman spectrum[21] reported for **10**; NMR (CCl_4) δ 0.40–0.60 (m, 4 H), 1.10 (m, 1 H), 1.52 (s, 6 H).

B. Radical Conditions. Reactions were carried out at −15 °C on a solution which was 0.50 mole fraction in **4** (250 mg of **4** in 300 mg of CCl_4). Oxygen was removed by bubbling nitrogen gas through the reaction mixture for ca. 3 min. The reaction flask was illuminated with a 275-W General Electric lamp. Chlorine (20 μl) was distilled into the stream of nitrogen carrier gas. The crude reaction mixture was analyzed by NMR as described above (30% yield), and found to contain products **7**, **8**, **9**, and **10** in a ratio of 2.1:1.0:1.8:1.4, respectively.

Isomerization of 7. To 700 mg of dichloride **7** in 0.5 ml of reagent acetone was added 50 mg of fused $ZnCl_2$.[12] After 30 min at room temperature the reaction mixture was poured into 15 ml of water and the products were isolated as described above for the isomerization of **2a**. An NMR spectra of the crude oil showed that the products **12**-(*Z*) and **12**-(*E*) were formed in a ratio of 1:5, respectively.[19] Distillation gave 0.560 g (80%) of the mixture (bp 73–76 °C, at 8.0 mm) with the following spectral properties: ir (neat) 3010 (C–H), 2960 (C–H), 1660 (C=C), 1440 and 1380 (C–H), 1290, 1260, 1160, 1080, 940, 910, 830, 810, 790, 720, 680 cm^{-1}; NMR (CCl_4) δ 1.78 and 2.00 (two quartets, J = 0.8 and 1.0 Hz, respectively, 3 H), 2.53 (q, J = 6.8 Hz, 2 H), 3.46 (t, J = 6.8 Hz, 2 H), 3.97 (br s, 2 H), 5.55 (m, 1 H).

Reaction of Hydrochloric Acid with 4. To 820 mg of **4** in 30 ml

of methylene chloride at −15 °C was bubbled HCl gas for 1 min. The reaction mixture was allowed to warm to room temperature and the solvent was then removed on a rotary evaporator. Analysis of the crude mixture by NMR showed only **10** and unreacted **4**. Distillation gave 660 mg of pure **10** [bp 45–47 °C, 60 mm (lit.[22] 104–105 °C, 760 mm)] with the properties reported above.

Isomerization of 10. To 600 mg of **10** in 2.0 ml of anhydrous ether was added 50 mg of fused $ZnCl_2$.[12] The reaction mixture was stirred for 5 h at 25 °C. Workup as described for the isomerization of **2a** above gave pure **11** [bp 82–83 °C, 100 mm (lit.[22] 131–133 °C, 760 mm)] with the same spectral properties reported for 5-chloro-2-methyl-2-pentene.[22]

Reaction of Methyl Hypochlorite with 4. A. Ionic Conditions. Oxygen was bubbled through a solution of 585 mg (7.15 mmol) of **4** in 13.5 ml of anhydrous methanol at 0 °C for 2 min. To this stirred solution, under an oxygen atmosphere, in the dark, was added dropwise 4.0 ml of a 1.4 M methyl hypochlorite solution in methylene chloride. The reaction mixture was poured into 100 ml of ice water, extracted with methylene chloride, and dried over $MgSO_4$. The yield by NMR analysis of the crude mixture using benzene as an internal standard showed the products to be formed in 75% yield. The product ratios were 1.0:1.2:5.0 for **8, 9,** and **13,** respectively. Distillation gave pure **13** (bp 70–72 °C, 24 mm) with the following spectral properties: ir (neat) 3080 (c-C_3H_5), 2950 (C–H), 1460 and 1375 (C–H), 1100 (C–O), 1013 (c-C_3H_5), and 750 cm^{-1}; NMR (CCl_4) δ 0.20–0.60 (m, 4 H), 0.7–1.1 (m, 1 H), 1.05 (s, 3 H), 3.24 (s, 3 H), 3.44 (s, 2 H). A similar reaction was carried out at 25 °C for 3 h in methylene chloride as the solvent. The solvent was removed on a rotary evaporator at room temperature. Analysis by NMR showed the product ratio for **7**,[23] **8, 9,** and **13** to be 1:5:4:5, respectively. Product **13** (100 mg) was found to be stable when treated with 30 mg of fused $ZnCl_2$ in 0.3 ml of anhydrous ether at 25 °C for 48 h.

B. Radical Conditions. Reactions of methyl hypochlorite under radical conditions were carried out at the mole fractions of **4** in methylene chloride listed in Table II. To 655 mg (8.0 mmol) of neat **4** at 0 °C, under nitrogen and ultraviolet illumination, was added 4.0 ml of a 0.08 mole fraction (1.4 M) methyl hypochlorite solution in methylene chloride. The solvent was removed at reduced pressure and NMR analysis showed only product **14.** Product **15** was also formed when the reaction was carried out under dilute conditions (Table II). Distillation gave pure **14** (76%) (bp 56–60 °C, 20 mm): ir (neat) 3080 (c-C_3H_5), 2950 (C–H), 1450 and 1380 (C–H), 1270, 1105 (C–O), 1015 (c-C_3H_5), 815, and 760 cm^{-1}; NMR (CCl_4) δ 0.30–0.70 (m, 4 H), 0.9–1.2 (m, 1 H), 1.46 (s, 3 H), 3.36 (s, 3 H), 3.42 (s, 2 H).

Isomerization of 14. To 0.500 g of **14** in 1.0 ml of anhydrous ether was added 60 mg of fused $ZnCl_2$.[12] The reaction mixture was stirred for 5 min at 25 °C and then isolated as described above for the isomerization of **2a.** Analysis by NMR on the crude mixture showed **15**-(*Z*) and **15**-(*E*) to be formed in a ratio of 1:4, respectively.[19] Distillation gave 0.405 g of the mixture **15**-(*Z*) and **15**-(*E*) (81%) (bp 115–121 °C, 25 mm): ir (neat) 3000 (C–H), 2940 (C–H), 1440 and 1430 (C–H), 1295, 1190, 1110, 1095, 790, 765, 715, and 660 cm^{-1}; NMR (CCl_4) δ 1.63 and 1.76 (br singlets, 3 H), 2.53 (q, J = 7.0 Hz, 2 H), 3.20 (s, 3 H), 3.47 (t, J = 7.0 Hz, 3 H), 3.72 (br s, 2 H), 5.35 (m, 1 H).

Reaction of Iodobenzene Dichloride with 4. A. Ionic Conditions. The reaction mixture [0.006 mole fraction **4** (3.0 mmol) in methylene chloride as solvent] was prepared at 0 °C, in the dark, under O_2, as described for the ionic reaction of methyl hypochlorite above. IBD (0.9 mmol) was added as a solid. The reaction mixture was allowed to come to room temperature and then stirred under an oxygen atmosphere for 20 h. Removal of the solvent on a rotary evaporator at room temperature followed by NMR analysis showed the products (70%) **7**,[23] **8, 9, 10,** and **12** to be formed in a ratio of 6.3:1.3:1.0:1.1:4.6, respectively.

B. Radical Conditions. The reactions were carried out under the radical conditions described for the reaction of methyl hypochlorite to **4** above. To IBD (3.0 mmol) in methylene chloride at 25 °C (mole fractions given in Table I) was added 0.5 ml of a 6.0 M solution of **4** in methylene chloride. The reaction mixture was stirred for ca. 3 min and the solvent was removed as described above. Analysis by NMR gave yields of ca. 75%. The product ratios[23] for each dilution are given in Table I.

Reaction of Trichloroamine with 4. To 265 mg (3.2 mmol) of **4** in methylene chloride or carbon tetrachloride (mole fraction **4** given in Table I) at −15 °C was added dropwise 2.7 ml of a 0.34 M solution of NCl_3 in methylene chloride or carbon tetrachloride. The reaction was carried out under the ionic and radical contions described above. The solvent was removed at room temperature on a rotary evaporator after all the NCl_3 was added. Analysis by NMR on the crude mixture showed yields of ca. 95%. The product ratios[23] are given in Table I.

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Registry No.—**1,** 693-86-7; **2a,** 58673-27-1; **2b,** 58673-28-2; **3a,** 58673-29-3; **3b,** 58673-30-6; **4,** 4663-22-3; **5,** 58673-31-7; (*Z*)-**6,** 58673-32-8; (*E*)-**6;** 58673-33-9; **7,** 58673-34-0; **8,** 5296-54-8; **9,** 42161-98-8; **10,** 58673-35-1; **11,** 7712-60-9; (*Z*)-**12,** 58673-36-2; (*E*)-**12,** 58673-37-3; **13,** 58673-38-4; **14,** 58673-39-5; (*Z*)-**15,** 58673-40-8; (*E*)-**15,** 58673-41-9; bromine, 7726-95-6; chlorine, 7782-50-5; methyl hypochlorite, 593-78-2; hydrochloric acid, 7647-01-0; iodobenzene dichloride, 932-72-9; trichloroamine, 10025-85-1.

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(3) (a) For example, Richey and Richey [*J. Am. Chem. Soc.*, **88,** 4971 (1966)] found that acid-catalyzed exchange of the hydroxyl group of methylcyclopropylmethanol is about 10^3 times faster than formation of rearranged products; and dehydration of 2-cyclopropyl-2-propanol gives 2-cyclopropylpropene[17] in good yield. In fact, most of the solvolysis data for homoallyl derivatives can be explained on the basis of a cyclopropylcarbinyl cation intermediate. (b) For a discussion see "Carbodium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1974, Chapters 23, 24, and 25. (c) M. Hanack, *Suom. Kemistil.*, **39,** 93 (1966); M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6,** 666 (1967). Solvolysis of 4-methyl-3-penten-1-ol tosylate gives 2-cyclopropylpropene: J. B. Rogan, *J. Org. Chem.*, **27,** 3910 (1962). For a review in the steroid system, see N. L. Wendler in "Molecular Rearrangements", Part 2, P. de Mayo, Ed., Interscience, New York, N.Y., 1964, Chapter 16. The homoallyl cation collapses without activation in the gas phase to the bisected cyclopropylcarbinyl cation; see W. H. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **94,** 5917 (1972).

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(10) Rearrangement of the 1,2 products to the 1,4 products was substantial in the VPC even when on column injection, or when a glass-lined injector oven was used.

(11) Slobodin[11] treated the reaction mixture **2a** and **3a** with base and obtained cyclopropylacetylene in 94% yield. Because of the high yield, Slobodin assumed that both **2a** and **3a** reacted to give cyclopropylacetylene. We repeated this reaction and found that cyclopropylacetylene was formed in high yield from **2a,** but no volatile products were found when **3a** was treated with base under the same conditions.

(12) Structural assignments of the products are based on their spectral properties and rearrangement of the 1,2 products to the 1,5 products with zinc salts. For rearrangement of cyclopropylcarbinyl alcohols and 1,2-dihalides with zinc salts, see M. Julia, Y. Noel, and R. Guegan, *Bull. Soc. Chim. Fr.*, 3742 (1968); M. Julia and Y. Noel, *ibid.*, 3749, 3756 (1968); A. N. Pudovik, *Zh. Obshch. Khim.*, **19,** 1179 (1949); *Chem. Abstr.*, **44,** 1005 (1950).

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(18) Distillation was discontinued after about one-third of the product distilled because of extensive decomposition in the distilling flask.
(19) The configurations of the *E* and *Z* isomers were assigned on the basis of their NMR spectra. The chemical shift of a methyl group in a trisubstituted olefin generally resonate about 0.1 ppm downfield when the methyl group is in a cisoid configuration relative to the vinyl hydrogen. The allylic coupling of the methyl group with the vinyl hydrogen is generally larger in the cisoid configuration by approximately 0.3–0.6 Hz. See L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Elmsford, N.Y., 1969, pp 225 and 316.
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(23) Control experiments showed that **7** was stable under the reaction conditions.

Kinetics of the Hydrolysis of Fluoromethyl Methyl Ether in Neutral to Alkaline Solution[1a]

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The kinetics of the hydrolysis of fluoromethyl methyl ether have been determined in aqueous solution at 25 °C in the pH range 7–13 by following the rate of release of hydrogen ions. The reaction is simple first order with k = 1.6–2.1 × 10^{-3} s^{-1} and shows no mass law effect in the presence of 0.1 M NaF. The mechanisms of hydrolysis consistent with these facts are discussed and compared to those for chloromethyl methyl ether, bis(chloromethyl) ether, and glycosyl halides.

As a part of a study of the stepwise mechanisms of carbonyl group addition–elimination reactions, we initiated a study of the kinetics of the hydrolysis of fluoromethyl methyl ether (FME). In particular, we had hoped to establish the relative reactivities of various nucleophiles toward the methoxymethyl cation as a model for nucleophilicity toward a protonated carbonyl group. In the limited study reported here this goal has not been realized, and further work has been postponed at least temporarily because of the demonstrated carcinogenic nature of the related chloromethyl methyl ether, which is used as the starting material for the preparation of the title compound, and the possible toxicity of FME itself.[2] However, since there are no reports (known to us) of quantitative studies of the hydrolysis of simple α-fluoroalkyl ethers, these results are of interest for comparison with the hydrolysis of chloromethyl methyl ether,[3] and with the chemical[4] and enzymatic[5] hydrolyses of glycosyl fluorides.

Experimental Section

Preparation and Characterization of Fluoromethyl Methyl Ether. The method of preparation is that of Via,[6] and is similar except for solvent to that described by Tullock and Coffman.[7] A total of 70 g (0.9 mol) of chloromethyl methyl ether (Eastman) was added over a period of 12 h to a refluxing suspension of 82 g (2 mol) of sodium fluoride (Baker analytical reagent, powder form) in 500 ml of purified[8] acetonitrile. A small distillation head was mounted atop the reflux condenser, and the low-boiling FME collected with a dry ice cooled Dewar condenser, with the collection flask also cooled by dry ice. About 25 ml of a water-white product was collected in this way, then transferred to and sealed in Pyrex ampules, and stored at −20 or −70 °C. The above operations were carried out with a nitrogen atmosphere.

The product thus obtained is very temperature sensitive. If the ether was allowed to stand (in a sealed vessel) at 0 °C for a short time, the color of the product changed to yellow and then deep red. Even at −20 °C the material in the ampules took on a yellow color (unless a small amount of triisopropylamine had been added). Furthermore, attempts to use a "cow" type distilling receiver resulted in decomposition of the product and deposition in the receiver of a white solid (uncharacterized, but probably paraformaldehyde).

The FME used in the analyses and in the kinetics experiments described below was redistilled in a trap-to-trap manner at atmospheric pressure under nitrogen, with the receiver cooled with liquid nitrogen and the pot in ice. In some cases a small amount of triisopropylamine was added to the pot since this seemed to aid the distillation. The redistilled ether was stored at −70 °C. For the kinetic studies described below, a solution of FME in anhydrous methanol was prepared by adding 5 ml of dry ice chilled methanol to about 1.5 ml of redistilled FME and was stored at −78 °C in a 14/20 ⅋-stoppered heavy-walled test tube.

The purity of the redistilled FME was checked by GLC and ^{1}H NMR analyses. With an Aerograph Hy-Fy gas chromatograph, which has a hydrogen-flame detector, we found that we could obtain excellent resolution of reactants and products using a 5 ft × 0.125 in. column of 15% XF-1150 on 60–80 Chromosorb W at room temperature. Samples were introduced by using a dry ice cooled 10-μl Hamilton syringe to quickly take an aliquot of ether from a dry ice–acetone cooled flask and inject it into the chromatograph. The redistilled FME yielded four well-resolved peaks that in order of increasing retention time had relative areas of 15:3:1:~0.1. The first peak is assumed to be due to FME. The second and third peaks have retention times identical with those of dimethoxymethane and acetone, respectively. The fourth peak was not assigned, but it was demonstrated that this peak was not due to chloromethyl methyl ether, acetonitrile, or methanol. GLC analysis of the chloromethyl methyl ether starting material showed that it contained a small amount of a contaminant with the same retention time as dimethoxymethane. The acetone in the product probably arose from the opening of the flask containing the fluoro ether while it was suspended in a dry ice–acetone bath, since it did not come from the cooling of the syringe.

The ^{1}H NMR spectrum of a mixture of the redistilled FME plus Me_4Si in a tightly stoppered heavy-walled NMR tube was obtained at about −50 °C using a Varian A-60 NMR spectrometer. The spectrum is consistent with the structure of FME, and indicates very small amounts of dimethoxymethane and acetone contaminants. Observed peaks were assigned as follows: A singlet at δ 2.17 was increased in size by the addition of acetone and is therefore assigned to hydrogens of