Radiation-Initiated Codimerization of Methallyl Chloride with Unsaturates

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Ionizing radiation initiates the codimerization of methallyl chloride with a variety of unsaturated compounds including 1-pentene, maleic anhydride, allyl acetate, and vinyl acetate. The general product from this free-radical reaction with unsaturate, $CH_2{=}CHR$, is a codimer, $Cl(CH_2CHR)CH_2C(CH_3){=}CH_2$. With favorable reaction conditions (150°, 0.1 Mrad/hr), G values for codimer formation range from 50 to 250. Higher molecular weight trimers of the general structure $Cl(CH_2CHR)_2CH_2C(CH_3){=}CH_2$ and $CH_3C(CH_2Cl)_2(CH_2CHR)CH_2C(CH_3){=}CH_2$ may also be formed. A major side reaction is the formation of methylallyl chloride dimer. A free-radical chain reaction is proposed for the codimerization, and ratios of rate constants for a number of the intermediate reaction steps have been determined from the product distributions resulting from variation of the methallyl chloride–unsaturate mole ratios.

While considerable attention has been devoted to the dimerization of the halogenated olefins trichloroethylene,[1-4] *cis*- and *trans*-dichloroethylene,[2] methallyl chloride,[2,5] allyl chloride,[2] and allyl bromide,[6] little work has been reported on the codimerization of halogenated olefins with nonhalogenated olefins.[7] The present paper describes the radiation-initiated codimerization of methallyl chloride (MAC) with a variety of unsaturated compounds.

Results

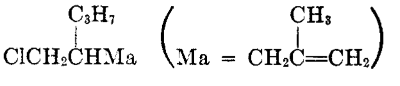
Methallyl Chloride and 1-Pentene.—Two typical product distributions from the radiation-initiated codimerization of methallyl chloride and 1-pentene at 150° are shown in Table I. The two principal products are the known methallyl chloride dimer,[5] 2-methyl-4,4-bis(chloromethyl)-1-pentene, and a codimer with the structure shown below. The structural

TABLE I

PRODUCT COMPOSITIONS FROM RADIATION-INITIATED CODIMERIZATION OF METHALLYL CHLORIDE AND 1-PENTENE AT 150° AND 0.1 MRAD/HR[a]

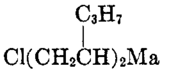
	[1-Pentene]/[methallyl chloride]			
	2/1		1/1	
Product	Wt %	G[b]	Wt %	G[b]
1-Pentene	57.6		44.2	
Methallyl chloride	31.3		36.8	
Codimer	4.33	160	6.54	241
Methallyl chloride dimer	2.31	76	6.54	214
A:A:B trimer	1.62	41	1.62	42
A:B:B trimer	0.94	22	1.58	37
Unidentified (three components)	1.70		1.99	

[a] Total dose was 1.62 Mrads. [b] Molecules formed per 100 ev absorbed by mixture.



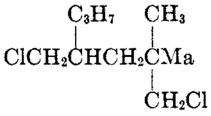
$$\mathrm{ClCH_2\overset{\overset{C_3H_7}{|}}{C}HMa}\quad\left(\mathrm{Ma} = \mathrm{CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2}\right)$$

assignment is based on mass spectral, nmr, and infrared analyses. In addition, two trimeric products were isolated and shown to have the following structures.



$$\mathrm{Cl(CH_2\overset{\overset{C_3H_7}{|}}{C}H)_2Ma}$$

A:A:B trimer



$$\mathrm{ClCH_2\overset{\overset{C_3H_7}{|}}{C}HCH_2\underset{\underset{CH_2Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}Ma}$$

A:B:B trimer

The direct effect of temperature and inverse effect of dose rate on the product yields are illustrated in Table II. On the basis of these results a dose rate of 0.1 Mrad/hr and 150° were chosen as standard reaction conditions. The effect of the composition of the mixture on product yields is summarized in Table III. These data show a dramatic increase in the yields of the methallyl chloride dimer and codimer with increasing concentration of methallyl chloride. The total G value for all products is >1100 at a methallyl chloride mole fraction of 0.68 (72 wt %) indicating a long kinetic chain length under these conditions. The rapid increase in G value for methallyl chloride dimer formation suggests a high G value for dimer formation in pure methallyl chloride (this point is verified in a later section).

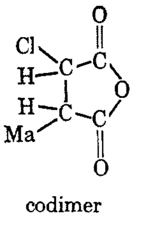
TABLE II

EFFECT OF TEMPERATURE AND DOSE RATE ON PRODUCT YIELDS FROM METHALLYL CHLORIDE AND 1-PENTENE[a]

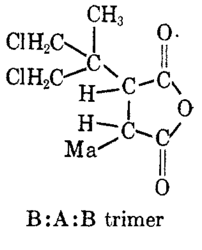
	Temp, °C		
	100	150	150
	Dose rate, Mrads/hr		
Product	0.1	0.1	0.89
G (codimer)	22	71	17
G (methallyl chloride dimer)	6.7	20	4.7
G (A:A:B trimer)	9.3	26	6.0
G (A:B:B trimer)	2.6	7.3	1.6
ΣG	40.6	124.3	29.3

[a] [1-Pentene]/[methallyl chloride] = 4/1.

Methallyl Chloride and Maleic Anhydride.—Codimerization of methallyl chloride with maleic anhydride was investigated because maleic anhydride has a strong tendency to alternate in copolymerization reactions. The products isolated included methallyl chloride dimer, the codimer, and a single trimer. The structures of the codimer and trimer are shown below. In addi-



codimer



B:A:B trimer

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[1] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[2] C. E. Frank and A. U. Blackham, *ibid.*, **72**, 3283 (1950).

[3] A. Roedig and R. Kloss. *Chem. Ber.*, **90**, 2906 (1957).

[4] A. J. Blardinelli and W. H. Yanko, U. S. Patent 2,961,388 (Nov 22, 1960).

[5] K. E. Wilzbach, F. R. Mayo, and R. Van Meter, *J. Am. Chem. Soc.*, **70**, 4069 (1948).

[6] M. S. Kharasch and G. Buchi, *J. Org. Chem.*, **14**, 84 (1949).

[7] J. R. Roland, British Patent 589,065 (June 10, 1947).

TABLE III
EFFECT OF METHALLYL CHLORIDE MOLE FRACTION ON PRODUCT DISTRIBUTION FROM CODIMERIZATION OF METHALLYL CHLORIDE WITH UNSATURATES

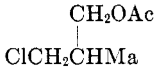
		G (product), methallyl chloride mole fraction					
Unsaturate	Product	0.09	0.20	0.33	0.50	0.67	0.88
1-Pentene[a]	Codimer	14	71	160	241	341	242
	MAC dimer	5.3	20	76	214	716	1650
	A:A:B trimer	6.8	26	41	42	28	7
	A:B:B trimer	0.7	7.3	22	37	69	50
			0.24	0.35	0.55	0.72	0.83
Maleic anhydride[b]	Codimer		163	256	238	113	55
	MAC dimer		...	...	41	209	493
	B:A:B trimer		21	100	267	423	382
			0.21	0.32	0.51		0.80
Allyl acetate[c]	Codimer		23	36	37		26
	MAC dimer		9.0	22	53		142
	A:A:B trimer		1.6	6.5	5.1		1.5
	A:B:B trimer		2.8	2.5	4.2		2.8
	B:A:B trimer		2.5	7.5	11		10
				0.36	0.50	0.74	0.84
Vinyl acetate[d]	Codimer			67	43	23	72
	MAC dimer			41	45	67	438
	B:A:B trimer			18	16	13	39

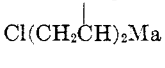
[a] 150°, 0.10 Mrad/hr. [b] 155°, 0.090 Mrad/hr. [c] 153°, 0.092 Mrad/hr. [d] 150°, 0.095 Mrad/hr.

tion to these products, a new product, 1,3-dichloro-2-methylpropane was detected.

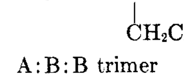
The effect of the composition of the mixture on the yields of the various products is summarized in Table III. The G values for the codimer and B:A:B trimer are high; 250 for the codimer at methallyl chloride mole fraction 0.35 (33 wt %), and 425 for the trimer at methallyl chloride mole fraction 0.72 (70 wt %). Significantly the G value for methallyl chloride dimer is low at mole fractions of methallyl chloride <0.60 and thus a combined selectivity to substituted succinic anhydrides (codimer and trimer) of 80% can be obtained at methallyl chloride mole fractions ranging from 0.35 to 0.60 with combined G values ranging from 350 to 525, respectively.

Methallyl Chloride and Allyl Acetate.—The codimerization of methallyl chloride and allyl acetate was investigated at 133 and 153°. The two principal products are methallyl chloride dimer and the codimer with the structure shown below. Three trimeric products were isolated and shown to have the following structures. Also small amounts of allyl chloride and allyl ether were found.

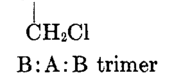

$ClCH_2\overset{\overset{\textstyle CH_2OAc}{|}}{C}HMa$


$Cl(CH_2\overset{\overset{\textstyle CH_2OAc}{|}}{C}H)_2Ma$

A:A:B trimer


$ClCH_2\overset{\overset{\textstyle CH_2OAc}{\diagdown}}{C}HCH_2\underset{\underset{\textstyle CH_2Cl}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}Ma$

A:B:B trimer


$CH_3\underset{\underset{\textstyle CH_2Cl}{|}}{\overset{\overset{\textstyle CH_2Cl}{|}}{C}}-CH_2-\overset{\overset{\textstyle CH_2OAc}{|}}{C}HMa$

B:A:B trimer

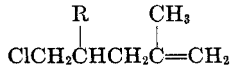
In Table III the G values for the formation of products at 153° are shown *vs.* methallyl chloride mole fraction. The G values are low, considerably smaller than in the methallyl chloride–1-pentene system, indicating a short kinetic chain length. The yields are reduced by a factor of 2 when the temperature is lowered to 133°.

Methallyl Chloride and Vinyl Acetate.—In an attempt to increase the kinetic chain length, the codimerization reaction was carried out with vinyl acetate, a reactive monomer with a high homopolymerization rate. The products include methallyl chloride dimer, the codimer, and a B:A:B trimer. Surprisingly little nonvolatile residue is formed, in most cases no more than with a control sample treated the same way without radiation. The effect of increasing methallyl chloride concentration on the product yields is shown in Table III. In contrast to the methallyl chloride–1-pentene system and the methallyl chloride–allyl acetate system, the yield of codimer passes through a minimum as the methallyl chloride concentration increases. The G values are considerably lower than those in the methallyl chloride–1-pentene system.

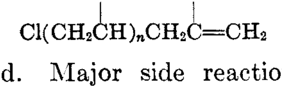
Methallyl Chloride.—The previous data for methallyl chloride codimerizations suggest that the G value for formation of methallyl chloride dimer in neat methallyl chloride should be large. This was confirmed by experiments at 150° at three dose rates. The G value increased from 655 at 0.87 to 18,000 at 0.0034 Mrad/hr. The dose rate dependence for G (methallyl chloride dimer) from these data is $1/I^{0.60}$ which is close to that expected for a free-radical chain reaction with bimolecular termination.

Discussion

Mechanism of Codimerization.—The net result of the codimerization reaction is the addition of methallyl chloride to an unsaturate, $CH_2{=}CHR$, to give the compound


$ClCH_2\overset{\overset{\textstyle R}{|}}{C}HCH_2\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2$

with the chlorine atom on C-1 and the methallyl group on C-2. "Telomers" with the general structure


$Cl(CH_2\overset{\overset{\textstyle R}{|}}{C}H)_nCH_2\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2$

may be formed. Major side reactions include the formation of methallyl chloride dimer and, in some

$$\text{MAC} \xrightarrow{\gamma} \text{Ma}\cdot + \text{Cl}\cdot$$

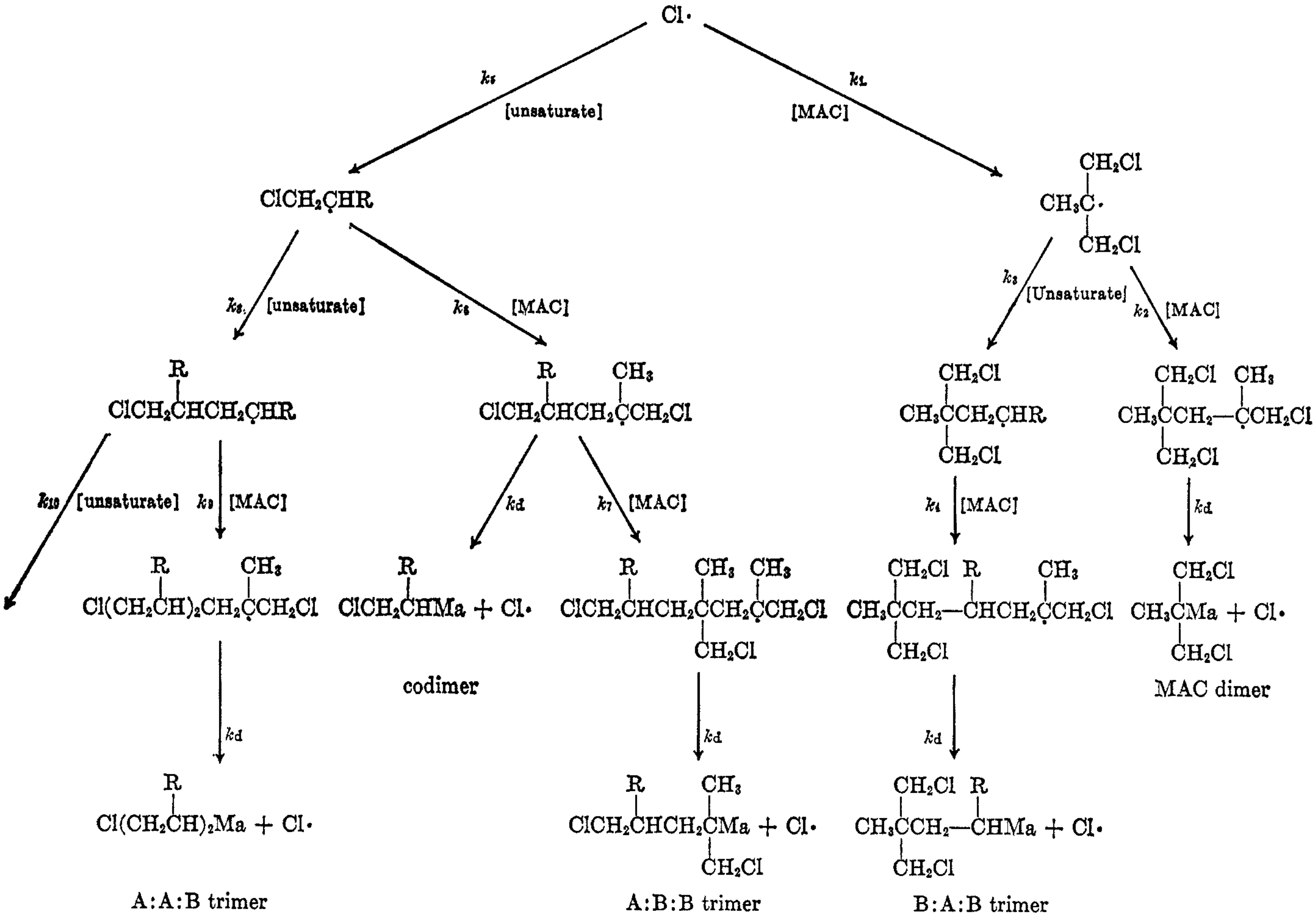
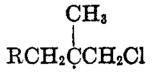


Figure 1.—Mechanism of the codimerization of methallyl chloride with unsaturates.

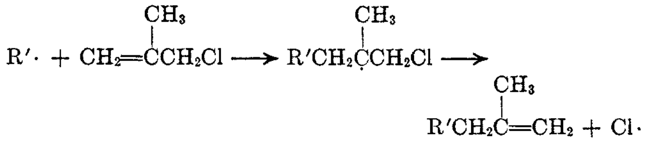
cases, two additional trimers. In analogy with the free-radical mechanism proposed for dimerization of halogenated olefins, a free-radical chain reaction is proposed for the codimerization of methallyl chloride with unsaturated compounds. The mechanism is summarized in Figure 1. The sequence of reactions, k_1 and k_2, leading to methallyl chloride dimer has been proposed by Wilzbach, Mayo, and Van Meter.[5] It is proposed here that the unsaturate, $CH_2{=}CHR$, can compete with methallyl chloride for the chlorine atom and the 1,3-dichloro-2-methylpropyl radical. Product formation can result when any intermediate radical adds to a methallyl chloride molecule to form a radical of the type



$$RCH_2\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}CH_2Cl$$

β elimination of the chlorine atom from this radical yields the unsaturated product and a chlorine atom to continue the chain. Alternatively, the chlorine atom may be transferred directly from the above radical to a double bond as suggested by Wilzbach, *et al.*[5]

Initiation by ionizing radiation is likely to be by direct scission of the weak allylic carbon–chlorine bond to give a chlorine atom. Other radicals produced by radiation can produce additional chlorine atoms by addition to methallyl chloride followed by β elimination.



$$R'\cdot + CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2Cl \longrightarrow R'CH_2\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}CH_2Cl \longrightarrow R'CH_2\overset{CH_3}{\overset{|}{C}}{=}CH_2 + Cl\cdot$$

Since initiation is due primarily to direct interaction of radiation or radiation-produced fragments with methallyl chloride, the G value for initiation should increase as the mole fraction of methallyl chloride increases. This increase in G initiation may be largely responsible for the general increase in the G values for product formation as the mole fraction of methallyl chloride increases (see Table III).

Termination is likely to be bimolecular dimerization or disproportionation of radicals. The strong inverse dependence of G values for product formation on the dose rate in the methallyl chloride–1-pentene system supports bimolecular radical termination.

Kinetic Data for Methallyl Chloride–Olefin Codimerizations.—Utilizing the mechanism summarized in Figure 1 and the yields of the various products as the methallyl chloride concentration changes (Table III), one can calculate the ratio of rate constants for most of the individual steps in the codimerization of methallyl chloride with 1-pentene, maleic anhydride, allyl acetate, and vinyl acetate. Thus the ratio of rate constants for the addition (or transfer) of chlorine atom to

TABLE IV

RATIOS OF RATE CONSTANTS AT 150°

Compd	k_5/k_1	k_2/k_3	k_8/k_6	k_d/k_7[a]
1-Pentene	1.31 ± 0.13		0.16 ± 0.02	33
Vinyl acetate	0.73 ± 0.06	2.3 ± 0.31		...
Allyl acetate[b]	0.73 ± 0.05	4.5 ± 0.81	0.15 ± 0.02	44
Allyl acetate[c]	0.72 ± 0.06	11.1 ± 2.6	0.058 ± 0.014	14
Maleic anhydride[d]	0.6 ± 0.2	0.18 ± 0.05		...

[a] Calculated at methallyl chloride mole fraction 0.50; k_d/k_7 is the ratio of a unimolecular and bimolecular rate constant and the units are moles per liter. [b] 153°. [c] 133°. [d] 155°.

unsaturate and methallyl chloride, k_5/k_1, can be calculated from

$$\frac{k_5}{k_1} = \frac{[\text{MAC}]}{[\text{unsaturate}]} \times \frac{\text{G (codimer)} + \text{G (A:A:B trimer)} + \text{G (A:B:B trimer)}}{\text{G (MAC dimer)} + \text{G (B:A:B trimer)}} \tag{1}$$

Similarly the ratio of rate constants for the addition of chloroalkyl radical, $ClCH_2\dot{C}HR$, to unsaturate and methallyl chloride, k_8/k_6, can be calculated from

$$\frac{k_8}{k_6} = \frac{[\text{MAC}]}{[\text{unsaturate}]} \frac{\text{G (A:A:B trimer)}}{\text{G (codimer)} + \text{G (A:B:B trimer)}} \tag{2}$$

Also the ratio of rate constants for the addition of the 1,3-dichloro-2-methylpropyl radical to methallyl chloride and unsaturate, k_2/k_3, can be calculated from

$$k_2 = \frac{[\text{unsaturate}]}{[\text{MAC}]} \frac{\text{G (MAC dimer)}}{\text{G (B:A:B trimer)}} \tag{3}$$

Finally, assuming that β elimination of a chlorine atom from $RCH_2\dot{C}(CH_3)CH_2Cl$-type radicals gives a free chlorine atom, the ratio of rate constants for the β elimination of a chlorine atom from $ClCH_2CHR-CH_2\dot{C}(CH_3)CH_2Cl$ to addition of this radical to methallyl chloride, k_d/k_7 can be estimated from

$$\frac{k_d}{k_7} = [\text{MAC}] \frac{\text{G (codimer)}}{\text{G (A:B:B trimer)}} \tag{4}$$

The ratios of rate constants calculated from the data in Table III are summarized in Table IV. The average deviations ranged from 10 to 15% (with the exception of k_d/k_7) when the ratios of rate constants for any unsaturated compound are calculated for three or more mole fractions of methallyl chloride. This supports the validity of the proposed mechanism for the codimerization reaction. The ratios of rate constants for the methallyl chloride–maleic anhydride mixtures are less accurate because of the high conversions, which change the mole ratio of methallyl chloride to maleic anhydride during the course of the reaction. Also included in Table IV are the ratios of rate constants calculated for the methallyl chloride–allyl acetate system at 133°.

The calculated values for the ratios of rate constants k_5/k_1 indicate little selectivity in the addition (or transfer) of chlorine atom to a variety of unsaturated compounds. The low selectivity tends to rule out direct transfer of chlorine atom from intermediate radicals to olefin. These data do suggest that the relative preference for the addition of chlorine atom is 1-pentene > methallyl chloride > vinyl acetate $\simeq$ allyl acetate > maleic anhydride. The chlorine atom is a reactive, electrophilic species and the addition to olefins is highly exothermic.[8] Thus the transition state for the reaction should resemble the reactants more closely than the products.[9] The order of addition of chlorine atom to the unsaturated compounds in this study is consistent with the decreasing electron density of the double bonds owing to the inductive effect of the substituents in the ground-state molecule. The fact that within experimental error, k_5/k_1 does not change with temperature in the methallyl chloride–allyl acetate system is consistent with the low energy of activation for the addition reaction; *e.g.*, the energies of activation for addition of chlorine atom to vinyl chloride, *cis*-dichloroethylene, and trichloroethylene are all 1.5 ± 1.0 kcal/mole.[10]

The calculated values for the ratios of rate constants k_2/k_3, indicate considerable selectivity for the addition of 1,3-dichloro-2-methylpropyl radical to the unsaturates. These data demonstrate that the relative preference for the addition of 1,3-dichloro-2-methylpropyl radical is maleic anhydride > methallyl chloride > vinyl acetate > allyl acetate.

In contrast to the other ratios of rate constants, k_d/k_7 values were found to depend upon composition, and increased linearly with increasing methallyl chloride concentration. The values of k_d/k_7 for codimerization with 1-pentene increase by a factor of 2.5 when the methallyl chloride concentration is increased from 1.7 to 8.8 moles/l. Similarly, k_d/k_7 for codimerization with allyl acetate increases fourfold at both 133 and 153°. A possible explanation for this effect is that solvent interaction with the transition state for β elimination is occurring, similar to that proposed by Walling, Padwa, and Wagner[11] in the analogous β-elimination reaction of alkoxy radicals, *i.e.*, *t*-butoxy radical yielding acetone and methyl radical. In that study it was found that chloro olefins apparently stabilize the transition state for β elimination of *t*-butoxy radicals thus increasing the rate of β elimination relative to hydrogen abstraction from cyclohexane.[11b] The results of the present study suggest that methallyl chloride is more effective in stabilizing the transition state for β elimination of chlorine than 1-pentene or allyl acetate.

Kinetic Chain Length.—The relative reactivities of intermediate radicals in the codimerization reaction are important in determining the relative yields of products; however, a quantity of more practical importance is the kinetic chain length, *i.e.*, the number of molecules of product formed per initiating radical. In a radiation-initiated reaction the kinetic chain length can be calculated by dividing the G value for

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(8) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 298.

(9) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(10) P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, **58**, 318 (1962).

(11) (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); (b) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).

product formation by the G value for initiation the latter quantity is usually about eight in hydrocarbon systems. In the absence of an accurate G value for initiation of the codimerization reaction the total G value for product formation is used as a measure of the kinetic chain length.

Two general observations can be made on the total G value for product. Firstly the total G values in individual methallyl chloride–unsaturate systems increase with increasing methallyl chloride mole fraction as shown in Table V. However this increase is probably due mainly to an increase in the G (initiation) and does not represent an actual increase in kinetic chain length. Secondly, the total G values for codimerization of the four unsaturates with methallyl chloride with identical initiation conditions (150°, 0.1 Mrad/hr, methallyl chloride mole fraction, 0.5) decrease in the order maleic anhydride $\simeq$ 1-pentene $\gg$ allyl acetate $\simeq$ vinyl acetate, and thus the kinetic chain length must decrease in this order.

TABLE V

EFFECT OF METHALLYL CHLORIDE MOLE FRACTION ON TOTAL G VALUE FOR PRODUCT FORMATION

Unsaturate	Sum of G (products) methallyl chloride mole fraction 0.25	0.50	0.80
1-Pentene	190	534	1600
Maleic anhydride	250	590	890
Allyl acetate	56	110	180
Vinyl acetate	130	100	530

Experimental Section

Infrared spectra were measured using a Perkin-Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. The control settings were resolution, 927; response, 1; gain, 6.5; speed, 5; and suppression, 2. Infrared spectra of samples were recorded as thin films squeezed between salt plates or as solutions in Spectro Grade solvents in 0.05-mm sodium chloride microcavity cells (Type D, Barnes Engineering Co.) using a 4 × beam condenser. Nmr spectra were measured on a Varian A-60 spectrometer. Gas–liquid partition chromatographs were obtained with an Aerograph Model 350B dual-column unit. The relative peak areas were assumed to represent relative per cent by weight. The absolute accuracy of the analyses is estimated to be within 10% with better accuracy for the relative values. Mass spectra were obtained using a CEC 21–103 mass spectrometer with an ionizing voltage of 70 v.

Reagents.—1-Pentene (Phillips Pure grade), allyl acetate (Eastman Organic Chemicals), and vinyl acetate (Union Carbide Chemical Co.) were purified by fractional distillation from calcium hydride through a 60-cm Piros–Glover spinning-band column in a nitrogen atmosphere. The purified materials were stored under nitrogen until used. Methallyl chloride (Shell Chemical Co.) was purified by preparative gas–liquid partition chromatography on a Ucon P/firebrick column (9.5-mm o.d. × 6 m long). Maleic anhydride (Matheson Coleman and Bell) was used with no further purification. The purified vinyl acetate and methallyl chloride were stored at −10° until used.

Codimerization Reactions.—Stock solutions consisting of accurately weighed amounts of methallyl chloride and the desired unsaturate were prepared. Aliquots (0.5–2 ml) were placed in 13 mm o.d. × 100 mm long heavy-walled Pyrex ampoules, degassed, and sealed *in vacuo*. The samples were irradiated at the desired temperature ±3° in a 10,000-curie cobalt-60 facility. The low dose rates (*ca.* 0.1 Mrad/hr) were determined by ferrous dosimetry while the high dose rates (*ca.* 1 Mrad/hr) were determined by ceric dosimetry. The total doses were varied to maintain low conversion and ranged from 0.6 to 6 Mrads. Control experiments were carried out at the same temperatures in the absence of radiation to determine the extent, if any, of thermal reaction.

Codimerization of Methallyl Chloride and 1-Pentene.—The products were analyzed by gas–liquid partition chromatography (glpc) using a Ucon P/firebrick column (6-mm o.d. × 1.5 m long) programmed from 40 to 200° at 6°/min with a helium flow rate of 85 cc/min. The retention times of the various components are 1-pentene (0.5 min, began programming), methallyl chloride (4.5 min), codimer (18 min), MAC dimer (24 min), A:A:B trimer (28 min), and A:B:B trimer (33 min). Identification of each product was accomplished by trapping the glpc-separated components and analyzing each one by mass and infrared spectrometry. Sufficient codimer was collected from repetitive trapping to obtain an nmr analysis. The nmr spectrum of the codimer (CCl_4, TMS reference) exhibited δ = 4.80 ($=CH_2$), 3.45 (CH_2Cl), 2.05 (allylic CH_2), 1.70 (allylic CH_3), 1.35 (CH_2), and 0.90 ppm (CH_3). The peak areas were consistent with the expected number and distribution of hydrogens for the structure of the codimer shown in the text and demonstrated that a methine hydrogen multiplet was buried under the allylic methylene and methyl hydrogen absorptions. The codimer exhibited an infrared spectrum with ν_{max}^{neat} 3050 (w), 2950 (s), 2900 (sh), 1650 (w) ($C{=}C$), 1465 and 1445 (m), 1380 (w), 1290 (w), 895 (s) ($\overset{|}{C}{=}CH_2$), 750 (vw), 725 (w), 705 (vw), and 680 (w) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 160 (parent, 1 Cl),[12] 124 (M − HCl), 117 (M − C_3H_7), 111 (M − CH_2Cl), 69, 56 ($C_4H_8^+$), 55 ($C_4H_7^+$), 43 ($C_3H_7^+$). The MAC dimer exhibited an infrared spectrum with ν_{max}^{neat} 3050 (w), 2950 (s), 2850 (sh), 1650 (w) ($C{=}C$), 1460 (m), 1440 (m), 1380 (m), 1290 (w), 955 (w), 900 (s) ($\overset{|}{C}{=}CH_2$), 830 (w), 788 (w), 740 (m), and 720 (w) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 180 (parent, 2 Cl), 144 (1 Cl, M − HCl), 131 (1 Cl, M − CH_2Cl), 124 (2 Cl, M − C_4H_8), 95, 93, 92, 89, and 56 ($C_4H_8^+$). The A:A:B trimer exhibited an infrared spectrum with ν_{max}^{neat} 3050 (w), 2995 (s), 2900 (sh), 1650 (w), ($C{=}C$), 1465 and 1450 (m), 1380 (w), 1290 (vw), 890 (s) ($\overset{|}{C}{=}CH_2$), 735 (sh), 725 (w), and 685 (w) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 230 (parent, 1 Cl), 187 (1 Cl, M − C_3H_7), 174 (1 Cl, M − C_4H_8), 165 (M − C_2H_5 and HCl), 151 (M − C_3H_7 and HCl), 146 (1 Cl, 187 − C_3H_7), 138 (174 − Cl), 125 (174 − CH_2Cl). The A:B:B trimer exhibted an infrared spectrum with ν_{max}^{neat} 3050 (w), 2995 (s), 2870 (sh), 1650 (w) ($C{=}C$), 1460 and 1440 (m), 1380 (m), 1295 (w), 890 (s) ($\overset{|}{C}{=}CH_2$), 775 (w), and 735 (m) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 250 (parent, 2 Cl), 214 (1 Cl, M − HCl), 207 (2 Cl, M − C_3H_7), 194 (2 Cl, M − C_4H_8), 185 (1 Cl), 147 (1 Cl), 145 (1 Cl, M − $ClCH_2\overset{|}{C}HC_3H_7$), 137 (M − $C_3H_7Cl_2$), 123 (M − $C_2H_9Cl_2$), 111 (M − $C_5H_7Cl_2$), 109, 69.

Codimerization of Methallyl Chloride and Maleic Anhydride.—The products were analyzed by glpc using a SE-30/Fluoropak column (6-mm o.d. × 1.5 m long) programmed from 40 to 220° at 10°/min with a helium flow rate of 60 cc/min. The retention times of the various components are methallyl chloride (2.3 min), 1,3-dichloro-2-methylpropane (4.7 min), maleic anhydride (7.5 min), MAC dimer (14.5 min), codimer (20 min), and B:A:B trimer (26 min). The products were also analyzed using a DC 710/Fluoropak column (6-mm o.d. × 3.0 m long) programmed from 50 to 225° at 6°/min with a helium flow rate of 60 cc/min. Using these conditions the codimer peak was split into two components with a ratio of *ca.* 10:1 with the smaller component appearing first. The general similarity of the infrared spectra of these two components suggests that they are the *cis* and *trans* isomers of the codimer. The various products were identified in the same manner as described above. The codimer exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2900 (w), 1855 (w) and 1780 (s) ($C{=}O$), 1640 (vw) ($C{=}C$), 1435 (w), 1410 (w), 1250 (m) ($C{-}O$), 1210 (w), 1065 (m), 1015 (m), 920 (m), 890 (w) ($\overset{|}{C}{=}CH_2$), and 800(m) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 188 (parent, 1 Cl), 111 (M − C_3H_6) and Cl, 99 (M − C_4H_6 and Cl), 91 (M − H_2CO_3 and Cl), 81 (M − C_2O_3 and Cl), 79, 67, 55, 53. The B:A:B trimer exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2900 (w), 1850 (w) and 1775 (s) ($C{=}O$), 1430 (w), 1380 (w), 1235 (sh), 1205 (w), 1065 (m), 1015 (w), 930 (s), 795 (w), 745 (m), and 725 (m) cm^{-1}; and mass spectrum with the following selected ions, *m/e* 278 (parent, 2 Cl), 223 (2 Cl, M − C_4H_7), 206 (2 Cl, M − C_2O_3), 157 (1 Cl, M − C_2O_3 and CH_2Cl). 1,3-

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[12] Where chlorine-containing species are observed, only the species with the most abundant chlorine isotope is listed.

Dichloro-2-methylpropane was identified from the infrared and mass spectra of glpc-trapped material.

Codimerization of Methallyl Chloride and Allyl Acetate.—The products were analyzed by glpc using a Ucon P/firebrick column (6 mm o.d. × 1.5 m long) programmed from 40 to 200° at 6°/min with a helium flow rate of 60 cc/min. The retention times of the various components are allyl chloride (2.7 min), methallyl chloride (4.5 min), allyl ether (6.5 min), allyl acetate (9.1 min), MAC dimer (24 min), codimer (27.4 min), B:A:B trimer (43.7 min), A:B:B trimer (47.5 min), and A:A:B trimer (52.8 min). The various products were identified in the same manner as described above. The codimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 3050 (sh), 2950 (s), 1745 (vs) (C═O), 1650 (w) (C═C), 1380 (m), 1365 (m), 1230 (vs) (C—O), 1030 (s) (C—O), 980 (w), 890 (m) ($\overset{|}{C}$═CH$_2$), 830 (w), 740 (sh), 725 (w), and 690 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 154 (M − HCl), 130 (1 Cl, M − $C_2H_4O_2$), 95 (130 − Cl), 43 ($C_2H_3O^+$). The A:A:B trimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 2900 (s), 1745 (vs) (C═O), 1380 (m), 1365 (m), 1225 (vs) (C—O), 1035 (s) (C—O), 980 (w), 895 (w) ($\overset{|}{C}$═CH)$_2$, 735 (w), and 695 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 230 (1 Cl, M − $C_2H_4O_2$), 170 [1 Cl, M − 2($C_2H_4O_2$)], 157 (1 Cl, M − $C_2H_4O_2$ and $C_3H_5O_2$), 135 ($C_{10}H_{15}^+$), 121 (157 − HCl), 96 ($C_7H_{12}^+$), 43 ($C_2H_3O^+$). The A:B:B trimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 3050 (w), 2900 (s), 1745 (vs) (C═O), 1650 (w) (C═C), 1385 (m), 1370 (m), 1225 (vs) (C—O), 1035 (s) (C—O), 892 (m) ($\overset{|}{C}$═CH$_2$), 840 (w), 775 (w), 740 (m), and 725 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 245 (1 Cl, M − Cl), 207 (2 Cl, M − $C_3H_5O_2$), 184 (1 Cl, M − $C_2H_4O_2$ and HCl), 96 ($C_7H_{12}^+$). The B:A:B trimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 2900 (s), 1745 (vs) (C═O), 1385 (m), 1370 (m), 1290 (w), 1225 (vs) (C—O), 1030 (s) (C—O), 980 (w), 890 (sh), 870 (m), 840 (m), 780 (w), 740 (m), 735 (w), and 700 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 245 (1 Cl, M − Cl), 220 (2 Cl, M − $C_2H_4O_2$), 207 (2 Cl, M − $C_3H_5O_2$), 182 (2 Cl, M − C_2H_3O and C_4H_7), 171 (1 Cl, M − $C_3H_5O_2$ and HCl), 95 ($C_7H_{11}^+$). Allyl chloride was identified by comparison of the infrared spectrum of the glpc-trapped sample with the authentic material (Shell Chemical Co.). Allyl ether was identified by comparison of the infrared spectrum of the glpc-trapped sample with the authentic material in the Sadtler Catalog.[13]

Codimerization of Methallyl Chloride and Vinyl Acetate.—The products were analyzed by glpc using a SE-30/firebrick column (6-mm o.d. × 1.5 m long) programmed from 40 to 225° at 6°/min with a helium flow rate of 60 cc/min. The retention times of the various components are vinyl acetate (4.3 min), methallyl chloride (6.5 min, programming started), codimer (29 min), MAC dimer (31.5 min), and B:A:B trimer (42.1 min). The codimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 3050 (w), 2950 (sh), 2920 (m), 1740 (s) (C═O), 1650 (w) (C═C), 1380 (m), 1225 (vs) (C—O), 1085 (w), 1035 (s) (C—O), 935 (m), 895 (s) ($\overset{|}{C}$═CH$_2$), and 740 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 127 (M − CH_2Cl), 116 (1 Cl, M − $C_2H_4O_2$), 81 ($C_6H_9^+$), 43 ($C_2H_3O^+$). The B:A:B trimer exhibited an infrared spectrum with $\nu_{\max}^{CS_2}$ 3050 (w), 2925 (m), 1740 (s) (C═O), 1640 (w) (C═C), 1360 (m), 1230 (s) (C—O), 1020 (m) (C—O), 893 ($\overset{|}{C}$═CH$_2$), and 740 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 211 (2 Cl, M − C_4H_7), 206 (2 Cl, M − $C_2H_4O_2$), 157 (1 Cl, M − $C_2H_4O_2$ and CH_2Cl), 81 ($C_6H_9^+$), 43 ($C_2H_3O^+$).

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[13] "Sadtler Catalog," Sadtler Research Laboratories, Philadelphia, Pa., 1959.

Stereochemistry of the Opening of Cyclopropanols[1]

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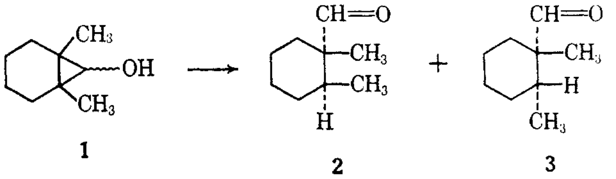
The stereochemistry of base-catalyzed opening of *endo*- and *exo*-7-hydroxy-1,6-dimethyl[4.1.0]bicycloheptane (1) was examined using potassium *t*-butoxide in *t*-butyl alcohol (both gave >90% retention) and ethylene glycol and its sodium salt (40 and 70% inversion). These results are consistent with those from previously reported electrophilic substitutions at carbon, implying that the three-membered ring does not introduce a significant novel mechanistic feature into the ring opening.

Nickon has reported that the conversion of 1-hydroxynortricylene to 2-norbornanone leads to >94% incorporation of an *exo*-deuterium atom at C-6 when various bases and deuterated solvents are used to effect the reaction.[2] This result of predominant inversion of stereochemistry at C-6 is unusual in that it does not conform to the pattern of stereochemical results obtained by Cram in his more general studies of electrophilic substitution at carbon, with carbon as a leaving group, using the same solvent systems.[3] In particular, Nickon observes predominant inversion and Cram predominant retention, with potassium *t*-butoxide in *t*-butyl alcohol. Nickon's result can be attributable either to a special feature of 1-hydroxynortricylene or to a special feature of cyclopropanols in general. That it is not the latter is clear from our results: we find that the stereochemistry of opening of *endo*- and *exo*-7-hydroxy-1,6-dimethyl[4.1.0]bicycloheptane (1) is in accord with the pattern observed by Cram,[3] namely, predominant retention (**1** → **2**) with potassium *t*-butoxide in *t*-butyl alcohol and much inversion (**1** → **3**) with ethylene glycol and its sodium salt. The only other study of the stereochemistry of cyclopropanol opening has been carried out by DePuy who finds predominant inversion in the opening of 1-methyl-*trans*-2-phenylcyclopropanol,[4] using only one medium,



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[2] A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963).

[3] For references and a summary of these studies, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 138–158.

[4] C. H. DePuy and F. W. Breitbeil [*J. Am. Chem. Soc.*, **85**, 2176 (1963)] described their compound as *cis*-1-methyl-2-phenylcyclopropanol.