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γ-Ray Induced Telomerization Reactions between Allylic Compounds and Carbon Tetrachloride. IV. Reactions of Acetates of Methyl-substituted Allylic Alcohols[*1]

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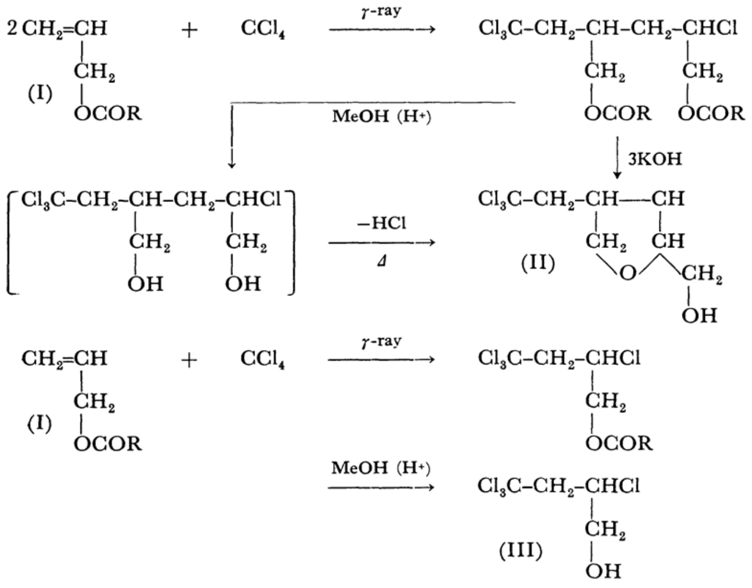
The γ-ray induced telomerization of allyl, α-methallyl, α,α-dimethylallyl, and β-methallyl acetates with carbon tetrachloride was carried out in order to compare the effects of methyl substituents. In the cases of the former three acetates, the effect of successive methyl substitution on the allylic α-position was found to show exactly the same regularity as to the effects on the velocities of C=C consumption, the telomer production ratios, and their change with the initial concentration of esters. In contrast with the case of α-substitution, while the β-methyl substituent retards the velocity of the C=C consumption to the utmost extent, it retards the telomer production ratio only a little; moreover, it depresses the effect of the ester concentration upon the former to some extent, but it minimizes that upon the latter. Together with these observations, the amounts of hydrogen chloride generated during irradiation was discussed in relation to the degradative chain transfer mechanism.

It has been reported[1] that 4-(β,β,β-trichloroethyl)tetrahydrofurfuryl alcohol (II) and 2,4,4,4-tetrachlorobutanol (III)[2] have been obtained in good yields by the methanolyses of the respective 2 : 1- and 1 : 1-telomers of allyl carboxylates (I), and that this method has been used to determine the "production ratios" of the telomers of some allyl carboxylates with high boiling points.

In this paper, the results will be reported of extending the above procedure to some acetates of α- and β-methyl-substituted allyl alchols. The effects of methyl substitutions, and of the concentrations of allylic esters on the velocities of double-bond consumption as well as on the production ratios of telomers were also studied in comparison with those of allyl acetate.

The allylic esters used were α-methallyl acetate (IV), α,α-dimethylallyl acetate (V), and β-methal-

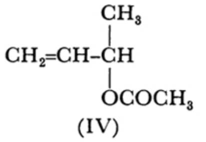


[*1] This work was presented at the 8th Conference of Radiation Chemistry, Tokyo, November, 1965, and in part at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966,

1) Part III: M. Okubo, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **88**, 212 (1967).

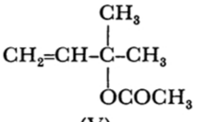
2) Regie nationale des usines Renault, French Pat. 1171147; *Chem. Abstr.*, **55**, 9283 (1961).

lyl acetate (VI). When 1 : 1- and 2 : 1-telomers



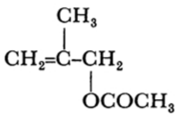
$CH_2{=}CH{-}\overset{CH_3}{\underset{OCOCH_3}{CH}}$

(IV)



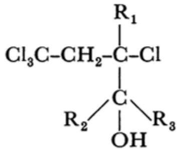
$CH_2{=}CH{-}\overset{CH_3}{\underset{OCOCH_3}{C}}{-}CH_3$

(V)

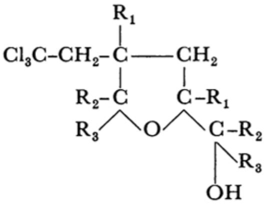


$CH_2{=}\overset{CH_3}{C}{-}\underset{OCOCH_3}{CH_2}$

(VI)



(VII)



(VIII)

are methanolyzed, they should give:

VIIa and VIIIa ($R_1=R_3=H, R_2=CH_3$) from IV,

VIIb and VIIIb ($R_1=H, R_2=R_3=CH_3$) from V, and

VIIc and VIIIc ($R_1=CH_3, R_2=R_3=H$) from VI respectively.

Experimental

Materials. Allyl acetate (I, $R=CH_3$), bp 103°C, was prepared from allyl alcohol and acetic acid.[3]

α-Methallyl acetate (IV), bp 112°C, was prepared by the esterification of α-methallyl alcohol with acetic anhydride. α-Methallyl alcohol, bp 96—98°C, was prepared in a 71% yield by the addition of methylmagnesium bromide to acrolein[4]. Methylmagnesium iodide gave a low yield (less than 40%).

α,α-Dimethylallyl acetate (V), bp 120°C, was obtained in a 64% yield by the successive addition of acetone[5] and acetic anhydride to a tetrahydrofuran solution of vinylmagnesium chloride. When α,α-dimethylallyl alcohol was isolated and esterified, the yield of the ester was lowered because of the rearrangement (to the γ,γ-dimethyl isomer), the decomposition (to isoprene and water), and its tertiary structure (causing steric hindrance).

β-Methallyl acetate (VI), bp 124°C, was prepared from acetic anhydride and β-methallyl alcohol.

γ-Ray Irradiation and Analysis of Products.[6] Solutions of the molar ratio of 1/5, prepared by adding 0.4 mol-portions of I ($R=CH_3$), IV, V, and VI respectively to 2.0 mol of CCl_4, were sealed into glass ampoules and irradiated at 25°C at the dose rate of 5.5×10^4 R/hr. After irradiation for a given number of hours, the ampoule was opened, and a small part of the CCl_4 solution was pipetted out and titrated with a KBr-$KBrO_3$ aqueous solution to determine the amounts of the unreacted allylic monomer. The total yields of telomers produced were weighed after distilling off the unreacted materials.

The mixtures of products obtained were fractionated under reduced pressure into 1 : 1- and 2 : 1-telomers and residues. All the telomer fractions were collected and redistilled, and the chlorine content, the molecular weights, and the infrared spectra were measured. The methanolysis products were analyzed in the same way as the telomers.

Solutions of molar ratios of 1/10 and of 1/2, prepared from 0.2 mol and/or 1.0 mol of esters and 2.0 mol of CCl_4, were investigated similarly.

Measurements of Generated Hydrogen Chloride. Into ampoules fitted with glass cooks, a CCl_4 solution of an allylic ester was sealed and irradiated. Another ampoule containing a small amount of distilled water was prepared and connected to the top of the irradiated one. The cock was opened, and the distilled water was introduced into the lower ampoule with shaking. After the aqueous layer was separated, the organic layer was washed with another small amount of distilled water. Aqueous fractions were collected and titrated by Volhard's method.

Results and Discussion

Analyses of Telomers. The boiling points, molecular weights, and chlorine contents of telomers were summarized in Table 1.

The table shows that products from I ($R=CH_3$), IV, and V are telomers with normal structures. In the case of VI, more hydrogen chloride was observed to be generated during distillation, thus causing somewhat lower values of the Cl-content and the molecular weight. This fact may indicate that the tertiary chlorine atom added to the β-carbon atom suffers thermal elimination more easily.

Methanolyses of Telomers. Results of the analyses of the methanolysis products are summarized in Table 2. In the columns of the calculated values, the numbers obtained by 1-mol-deacetylation from 1 : 1-telomers, and those obtained by 2-mol-deacetylation and 1-mol-dehydrochlorination from 2 : 1-telomers, are listed.

The yield of the methanolysis products of the 1 : 1-telomer of VI was as high as 73%, but on the analysis of the Cl-content by Stepanow's method, the reaction mixture was colored and the observed Cl-content was somewhat lower. This finding suggests that the reaction of metallic sodium with the sample was so vigorous that small fragments of the sample molecule escaped with the hydrogen gas generated and that a simultaneous resinification occurred.

As for the methanolysis product of the 2 : 1-telomer of VI, the Cl-content was found to be normal,

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[3] M. Ōkubo, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1191 (1966).

[4] L. Claisen, *Ber.*, **59**, 2344 (1926).

[5] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

[6] M. Ōkubo, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1196 (1966).

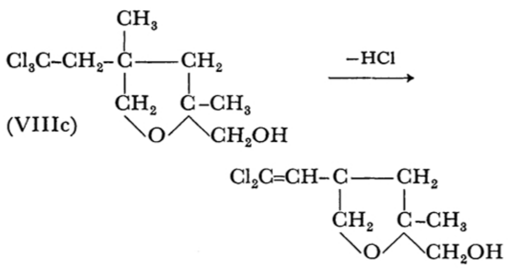
Table 1. Analyses of telomers

Allylic esters	1 : 1-Telomers Bp °C/mmHg	Mol wt obs.	Mol wt calc.	Cl-cont. obs.	Cl-cont. calc.	2 : 1-Telomers Bp °C/mmHg	Mol wt obs.	Mol wt calc.	Cl-cont. obs.	Cl-cont. calc.
I (R=CH_3)	102—105/5.0	251	254	55.1	55.8	183—185/5.0	349	354	39.5	40.1
IV	93— 95/2.5	263	268	51.5	52.9	164—168/2.5	377	382	35.6	37.2
V	102—105/2.5	278	282	49.2	50.2	178—180/2.5	407	410	33.9	34.6
VI	98—102/1.5	259	268	49.3	52.9	168—170/2.0	368	382	33.8	37.2

Table 2. Analyses of methanolysis products

Allylic Esters	Products from 1 : 1-Telomers Structures	Bp °C/mmHg	Mol wt obs.	Mol wt calc.	Cl-cont. obs.	Cl-cont. calc.	Products from 2 : 1-Telomers Structures	Bp °C/mmHg	Mol wt obs.	Mol wt calc.	Cl-cont. obs.	Cl-cont. calc.
I (R=CH_3)	III	97/5.0	210	212	65.9	66.9	II	130—132/4.0	231	233.5	45.9	46.3
IV	VIIa	102/5.0	219	226	62.5	63.6	VIIIa	134—137/3.0	260	261.5	39.9	40.7
V	VIIb	99/3.0	242	240	57.9	59.2	VIIIb	139/3.0	289	289.5	36.1	36.7
VI	VIIc	106/3.0	230	226	59.2	63.6	VIIIc	139—141/3.5	281—312	261.5	39.5	40.7

but the molecular weight was observed to increase gradually, being 281 48 hr and 312 72 hr after distillation. On the infrared absorption spectrum, new bands appeared at 1676, 1743, and 1788 cm^{-1}, showing the formation of a C=C bond. This seems to indicate that the dehydrochlorinated product may have a vinylidene chloride structure and may polymerize successively. Supposedly, the observed normal value of the Cl-content is due to the produced HCl trapped in the viscous sample.



Methanolysis products of other 2 : 1-telomers suffer the above changes much more slowly than that of VI. The product from allyl acetate changes only very slightly when standing for a year.

The infrared absorption spectra of the products from IV and V accorded with those of the methyl-substituted II and III respectively. Thus, it can be concluded that the methanolysis products of the respective telomers have VIIa, VIIb, VIIc, VIIIa, VIIIb, and VIIIc structures.

Velocities of C=C Consumption and Effects of Concentration. Esters, I, IV, V, and VI (0.4 mol), were dissolved in CCl_4 (2.0 mol) and irradiated at 25°C at a dose rate of 5.5×10^4 R/hr. The irradiation time, the percentages of C=C bonds consumed, the total yields of the telomers, and the amounts of reacted CCl_4 are shown in Table 3.

Table 3. Attempted reactions of allylic esters

Allylic esters	Irradn. time hr	C=C consumed %	Total yield of telomers g	CCl_4 reacted g
I (R=CH_3)	72	76	53.4	23.0
IV	96	70	52.2	18.4
V	120	57	47.3	20.5
VI	480	98	62.3	17.7

The velocities of C=C consumption, observed with each ester at concentrations of 1/5 and 1/10 under the same conditions, are shown in Fig. 1.

Table 3 shows that the irradiation times needed for the esters to arrive at the same degree of C=C consumption differ considerably. Drawing several straight lines parallel with the time-axis of Fig. 1, the points of intersection with each curve indicate the time necessary for the corresponding esters to come to the same degree of C=C consumption. Then, for each ester, the ratios of the times thus obtained at the initial concentration of 1/10 against that obtained for 1/5 are averaged:

Allyl acetate 2.0; α-Methallyl acetate 1.7; β-Methallyl acetate 1.5; α,α-Dimethylallyl acetate 1.3.

The value, 2.0, for allyl acetate is an interesting one in view of the mechanism of initiation, which needs further investigation. However, in the present discussion, this value can be used as a typical one in comparing the reactivities of the carboxylates of allylic alcohols. Therefore, the changeability of the velocities of the four esters with the initial concentration is in the following order:

Allyl > α-Methallyl > β-Methallyl > α,α-Dimethylallyl.

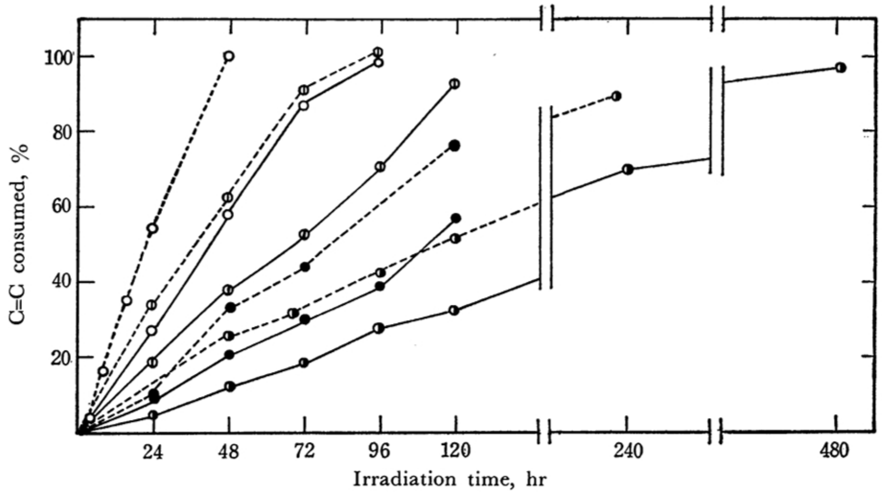


Fig. 1. Velocities of C=C consumption of four esters.
○: Allyl acetate, ○: α-Methallyl acetate, ●: α,α-Dimethylallyl acetate,
◑: β-Methallyl acetate.
——: Concentration of 1/5, - - -: Concentration of 1/10
Dose rate: 5.5×10^4 R/hr, at 25°C

On the other hand, the order of the bulkiness of the ester molecules is:

α,α-Dimethylallyl>
β-Methallyl—α-Methallyl>Allyl.

Consequently, it can be said that the changeability of the velocities with the initial concentration depends on the bulkiness of the ester molecules.

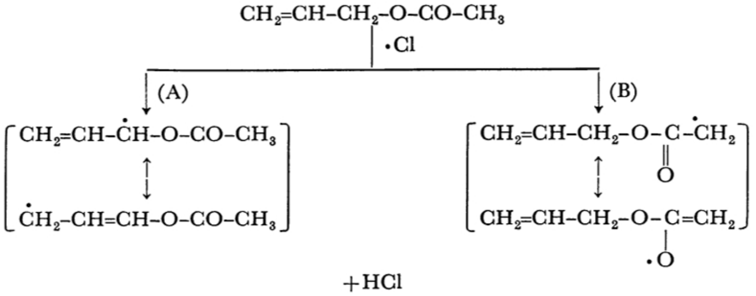
Although the following order of the velocities, at any initial concentration:

Allyl>α-Methallyl>α,α-Dimethylallyl>
β-Methallyl

(as shown in Table 3 and Fig. 1), displays a much larger steric hindrance by the methyl substituent on β-carbon (one of the reaction centers) than by those at α-carbon, it is remarkable that, in cases of successive α-methyl substitution, the three orders found above show the same regularity.

Results of the Measurement of HCl. Small quantities of hydrogen chloride were usually observed to be generated during the irradiation, but not in the case of α,α-dimethylallyl acetate.

Previously,[6] the relationship was discussed between the telomerization reaction and the degradative chain transfer,[7] which has been proposed to explain the low degrees of polymerization of allylic compounds. Since, under the present reaction conditions, a large number of CCl_4 molecules surround the allylic esters, the amounts of generated HCl could be used as a basis for estimating the degradative chain transfer. Two possible courses, (A) and (B), were presented:



The lack of generation of HCl in the case of the ester V suggests that HCl originates in α-hydrogen atoms of allylic groups and not in those of carboxyl residues. Therefore, the contribution of the course (B) is excluded in the present reaction. This conclusion is also supported by the fact that, in the cases of allyl acetate and allyl phenylacetate, no chloroform and no difference in the amount of HCl generated could be detected during irradiation.[6]

In order to inspect the reason for the strongly-retarding effect of the β-methyl substituent on the velocity, the amounts of HCl were measured in the

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[7] N. G. Gaylord and F. R. Eirich, *J. Am. Chem. Soc.*, **74**, 337 (1952); P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

cases of allyl and β-methallyl acetates. The results are summarized in Table 4. The amounts of HCl did not exceed 10% of the amount of the β-methallyl ester, which was observed to generate the largest amount of HCl among the present four esters. Therefore, it can be said that HCl-generation had no decisive effect upon the processes of the present reaction.

Table 4. Measurement of generated HCl
(Esters : 1/15 or 1/30 mol ; CCl_4 : 1/3 mol)

Experiment No.	Irradn. time *hr*	Allylic esters	Concn. molar *ratio*	C=C consumed %	HCl generated $\times 10^3$ mol
i	47	I ($R=CH_3$)	1/5	58.2	0.415
ii	95	I ($R=CH_3$)	1/5	97.6	0.800
iii	120	V	1/5	32.5	1.29
iv	240	V	1/5	64.6	2.50
v	480	V	1/5	97.8	4.76
vi	120	V	1/10	52.3	1.42
vii	240	V	1/10	90.0	2.50

Table 4 shows that the amounts of HCl have no reasonable relationship with : (1) the initial concentration, (2) the degree of C=C consumption, and (3) *the structures of the two esters ; however, it is* remarkable that the amounts are in an almost linear proportion to the irradiation time as seen in the order of the experiments :

$$i \rightarrow ii \rightarrow iii(vi) \rightarrow iv(vii) \rightarrow v$$

In the cases of the polymerization, Gaylord and Kujawa[8] discussed the ease of degradative chain transfer on the basis of the electron-donating character of the methyl substituent, which would stabilize the propagating radicals, produced *via* the course (A) to retard the reaction. However, their discussion is not straightforwardly applicable to explaining the results obtained. The only conclusion which can be drawn here is that the β-carbon, one of the reaction centers, is sterically much hindered against the approach of other molecules or radicals, and that then the addition reaction is retarded, *causing the generation of a relatively large amount* of HCl as the time elapses. This statement, however, does not preclude the possibility of the abstraction of the hydrogen atom from allylic α-carbon, causing HCl to be generated (degradative chain transfer) ; it only assigns the main effect upon the reaction velocity and the generation of HCl to the steric hindrance.

Telomer Production Ratios and Effects of Concentration. *The production ratios of 2 : 1-* and 3 : 1- to 1 : 1-telomers, obtained by the fractionation of each reaction mixture, are summarized in Table 5. The numbers in parentheses, calculated from the weights of distillation residues, are small and so can be regarded as near-approximations of the corresponding production ratios, except in the case of the concentration of 1/2 for allyl acetate.

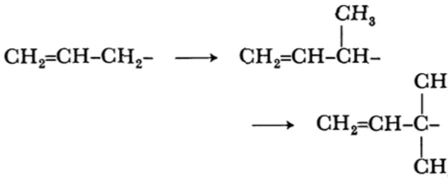
Table 5. Telomer production ratios

Allylic esters	Concn. molar ratio	C=C consumed %	Production ratios of telomers 1 : 1	2 : 1	3 : 1
I ($R=CH_3$)	1/2	74	1.0	10.0	(7.5)
I ($R=CH_3$)	1/5	85	1.0	5.7	(2.0)
I ($R=CH_3$)	1/10	84	1.0	2.9	(0.74)
IV	1/5	92	1.0	0.95	(0.06)
IV	1/10	95	1.0	0.40	(0.02)
V	1/5	85	1.0	(0.25)	—
V	1/10	90	1.0	(0.08)	—
VI	1/5	86	1.0	1.23	(0.42)
VI	1/10	98	1.0	0.75	(0.22)

Therefore, if the production ratios of 2 : 1- and 3 : 1- to 1 : 1-telomers are higher, the present ester *can be said to be more reactive, and the following* order is obtained for a concentration of either 1/5 or 1/10 :

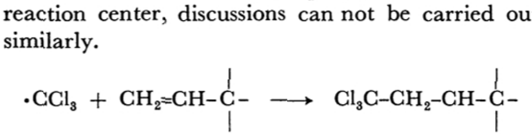
Allyl > β-Methallyl > α-Methallyl >
α,α-Dimethylallyl.

This order of reactivity, represented by the term of production ratio, is in accord with that of velocities except in the case of β-methallyl acetate. The fact *that the two orders are found to coincide when the* reaction centers have the same (vinyl) structure and when the neighbouring hydrogen atoms are substituted successively by methyl groups,

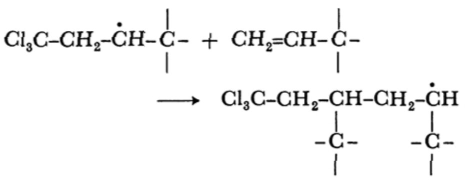


$$CH_2{=}CH{-}CH_2{-} \longrightarrow CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}}H{-} \longrightarrow CH_2{=}CH{-}\underset{CH_3}{\overset{CH_3}{C}}{-}$$

suggests that the steric hindrance of α-methyl groups may affect, to a similar extent, the two elementary reactions, (1) and (2). *On β-methallyl acetate,* which has a different (isopropenyl) structure in the reaction center, discussions can not be carried out similarly.



$$\cdot CCl_3 + CH_2{=}CH{-}\overset{|}{\underset{|}{C}}{-} \longrightarrow Cl_3C{-}CH_2{-}CH{-}\overset{|}{\underset{|}{C}}{-} \qquad (1)$$



$$Cl_3C{-}CH_2{-}\dot{C}H{-}\overset{|}{\underset{|}{C}}{-} + CH_2{=}CH{-}\overset{|}{\underset{|}{C}}{-} \longrightarrow Cl_3C{-}CH_2{-}\underset{-\overset{|}{\underset{|}{C}}-}{CH}{-}CH_2{-}\underset{-\overset{|}{\underset{|}{C}}-}{\dot{C}H} \qquad (2)$$

In any case, the yields of telomers of lower mo-

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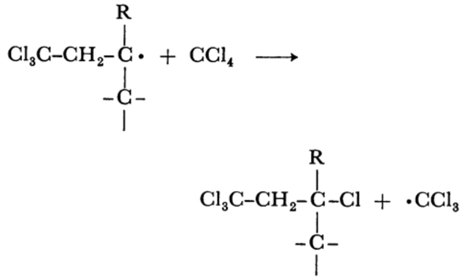
[8] N. G. Gaylord and F. M. Kujiwa, *J. Polymer Sci.*, **21**, 328 (1956).

ecular weights increased by a lowering of the initial concentration of esters, as may be seen in Table 5. This may be explained by the higher concentration of CCl_4 causing the rate of the reaction (3) to increase more than that of the reaction (2):



$$\mathrm{Cl_3C{-}CH_2{-}}\underset{\substack{|\\ -\mathrm{C}-\\ |}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}}\cdot + \mathrm{CCl_4} \longrightarrow \mathrm{Cl_3C{-}CH_2{-}}\underset{\substack{|\\ -\mathrm{C}-\\ |}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}}\mathrm{{-}Cl} + \cdot\mathrm{CCl_3} \qquad (3)$$

(R=H or CH_3)

Additionally, the ratios of the sum of 2:1- and 3:1-telomers at the concentration of 1/10 against that at the concentration of 1/5:

Allyl acetate 1/2.3; α-Methallyl acetate 1/24.; α,α-Dimethylallyl acetate 1/3.1; β-Methallyl acetate 1/1.6,

can be arranged in the very same order, in the case of successive α-substitution, as those formerly obtained for the velocities, for their change with the initial concentration, and for the production ratios. Therefore, it can be concluded that the successive α-substitution by a methyl group causes effects with the very same regularity.

In contrast with the case of α-substitution, the β-methyl substituent retards the velocity of C=C consumption to the utmost extent, but the telomer production ratio only a little; moreover, it depresses to some extent the effect of the ester concentration upon the former but it minimizes that upon the latter.

The author is indebted to Mr. Keichi Nunome of the present Institute for operating the γ-ray irradiator. The author also offers his gratitude to Professor Ryozo Goto of Kyoto University for his encouragement throughout the work.