Anal. Calcd. for $C_{12}H_8N_2I_2$: C, 33.21; H, 1.86; N, 6.46. Found: C, 32.96; H, 1.57; N, 6.64.

Hofmann reaction of o-iodobenzamide. To a solution of 0.06 cc. of bromine in 0.24 g. of sodium hydroxide and 2 cc. of water, prepared at 0°, was added 0.24 g. of powdered *o*-iodobenzamide. The mixture was stirred for 20 min. at 0°; most of the benzamide dissolved. Stirring was continued in the ice bath for another 1.5 hr., then the mixture was allowed to stand at room temperature for 1 hr. After decanting from a very small undissolved residue the mixture was heated at 80° for 2 hr. On cooling, the *o*-iodoaniline crystallized, m.p. 54–56°, yield 0.20 g.; acetyl derivative, m.p. 109.5–110.5°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. III. Relative Rates of Halogen Addition to Allylic Chlorides

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The magnitude of the deactivation of an ethylenic double bond by electron-attracting groups varies with the type, number, and position of the substituents. Thus, the relative reactivity toward addition of halogen decreases in the order: propene > allyl chloride > 3,3-dichloropropene > 3,3,3-trichloropropene. Isomers of the di- and trichloropropenes containing vinylic halogen were found to be less reactive. Allylic halides were found to add halogen approximately one thousand times faster than the corresponding vinylic halides.

Parts I and II of this series[2] described the additions of halogen compounds to allylic chlorides. This paper is concerned with a study of halogen addition to allylic chlorides. The influence of substituents on the rate of the addition of bromine to ethylenic compounds was investigated by Ingold and Ingold[3] and by Anantakrishnan and Ingold.[4,5] A competitive bromine addition method was used in the presence of methylene chloride at −35° and −78°. The reduced velocity for each ethylenic compound was obtained by comparing the rate of bromine addition of the compound with that of ethylene as unity,[5] *e.g.*, ethylene, 1.0; propene, 2.0; isobutylene, 5.5; trimethylethylene, 10.4; tetramethylethylene, 14.0.

Swedlund and Robertson[6] examined the rate of halogen addition to halogen derivatives of ethylenes. Chlorine was used instead of bromine for the determination of the relative rates which were obtained by comparing the k_2 values calculated at X = 50% (X = halogen absorption). The k_2 values were calculated from the curves by plotting the percentage of halogen absorption against time. The original values were revised in one of their later papers,[7] based on a new value for allyl bromide of 1.3×10^{-2} instead of 3×10^{-1}. (The revised values are included in Table II.)

This study was undertaken to investigate the influence of the number and position of electron-attracting substituents upon the reactivity of the double bond. The methods of preparation for the allylic chlorides used are given in Part I of this series. The kinetic method of Swedlund and Robertson[6] was employed for the rate studies. Vinyl bromide was used as the reference compound to correlate the data of this study with the values on relative rate given in their papers. Except for allyl chloride, chlorine was used instead of bromine to measure the rates of addition. In this type of study, iodine and its compounds are used for the determination of rates for the more reactive olefins; bromine is used for the moderately reactive olefins; and chlorine is commonly used for the less reactive olefinic compounds. The relative rates are obtained from comparisons of rates within one set of data and between one set and another irrespective of the halogen used, provided that there is a compound common to both sets. It has been found[8] that the rate ratio for chlorine and bromine addition, under a given set of conditions is about 250 to 1 and is not critically affected by the structure and reactivity of the olefin. The relative rates for a given pair of compounds are about the same regardless of whether they are determined by chlorine or bromine addition.

The results of the study of relative rates of halo-

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[1] This is an abstract of a part of the doctoral thesis submitted by Lieng-Huang Lee, Present address: Dow Chemical Company, Midland, Mich.

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TABLE I

Rates and Relative Rates of Addition of Chlorine to Allylic Chlorides

Compounds	Solvents	t (50%), min.	Rates (k_2) l. mole^{-1} min.$^{-1}$	Relative Rates ($CH_2{=}CH_2$ = 1.0)
Vinyl bromide[a]	HOAc	22.0	3.3×10^{-1}	1.3×10^{-5}
3,3-Dichloropropene	HOAc	11.0	6.7×10^{-1}	2.6×10^{-5}
cis-1,3-Dichloropropene	HOAc (10% H_2O)	7.3	1.0	2.5×10^{-6}
trans-1,3-Dichloropropene	HOAc (10% H_2O)	8.7	8.5×10^{-1}	2.1×10^{-6}
cis-Dichloroethylene[b]	HOAc (20% H_2O)	700.0	1.1×10^{-2}	4.4×10^{-9}
trans-1,3-Dichloropropene	HOAc (20% H_2O)	1.3	5.1	2.1×10^{-6}
3,3,3-Trichloropropene	HOAc (20% H_2O)	10.3	7.2×10^{-1}	2.9×10^{-7}
3,3,3-Trichloropropene	HOAc (40% H_2O)	1.5	4.9	2.9×10^{-7}
1,1,3-Trichloropropene	HOAc (40%) H_2O)	8.5	8.6×10^{-1},	5.1×10^{-8}

[a] Vinyl bromide was used as a standard and as a reference to standardize the method. [b] *cis*-Dichloroethylene value was used for comparison.[5]

gen addition to allylic chlorides are given in Table I. Table II is a summary of relative rates reported in the literature together with the values obtained in this study on the influence of electron-attracting substituents upon the rate of halogen addition.

TABLE II

Influences of Substituents on Relative Rates of Addition of Halogen to Olefinic Compounds

Compounds	Relative Rates	References
Propene	2.0	5
Ethylene	1.0	5, 6, 7
Allyl fluoride	3.4×10^{-2}	7
Allyl chloride	1.9×10^{-2}	7
Allyl bromide	1.3×10^{-2}	7
Allyl cyanide	2.7×10^{-3}	7
s-Dichloroisobutylene	2.4×10^{-4}	7
3,3-Dichloropropene-1	2.6×10^{-5}	
Vinyl bromide	1.3×10^{-5}	6
cis-1,3-Dichloropropene-1	2.5×10^{-6}	
trans-1,3-Dichloropropene-1	2.1×10^{-6}	
3,3,3-Trichloropropene-1	2.9×10^{-7}	
1,1,3-Trichloropropene-1	5.1×10^{-8}	
cis-Dichloroethylene	4.4×10^{-9}	6
trans-Dichloroethylene	2.2×10^{-9}	6
Trichloroethylene	1.3×10^{-11}	6

The effect of allylic halogen upon the reactivity of the double bond toward electrophilic addition of halogen is shown by the 100-fold decrease in rate for allyl chloride as compared to propylene. Introduction of a second allylic halogen, as in 3,3-dichloropene, gave a further 1000-fold decrease; and a third allylic halogen, as in 3,3,3-trichloropropene, gave another 100-fold decrease in the relative rate. One vinyl halogen is about as effective as two allylic halogens in decreasing the reactivity of the double bond toward halogen addition. The effect of vinylic and allylic halogen upon the relative reactivity of the double bond is compared in Table III. A 1000-fold difference in magnitude is shown in each case for a change of a single halogen from one type to the other in an otherwise identical structure. The theoretical implications of these relationships will be discussed in the concluding paper of this series.

TABLE III

Comparison of the Effect of Vinyl and Allylic Halogen upon the Relative Rates of Halogen Addition

Vinyl Halides	Allylic Halides	Difference in magnitude
$CH_2{=}CHX$, 10^{-5}	$CH_2{=}CH{-}CH_2X$, 10^{-2}	10^{-3}
$XCH{=}CHX$, 10^{-9}	$XCH{=}CH{-}CH_2X$, 10^{-6}	10^{-3}
$X_2C{=}CH{-}X$, 10^{-11}	$X_2C{=}CH{-}CH_2X$, 10^{-8}	10^{-3}

EXPERIMENTAL

A. *Addition of bromine. Reagents.* Dry bromine (Michigan Chemical Co.) was redistilled with potassium bromide. Acetic acid (Du Pont, ACS Standard) melted at 16.4–16.6°. The allylic chlorides: had the following b.p.'s allyl chloride (45°, 760 mm.), 3,3-dichloropropene (81–82.5°, 742.5 mm.) and 3,3,3-trichloropropene (45°, 103 mm.).

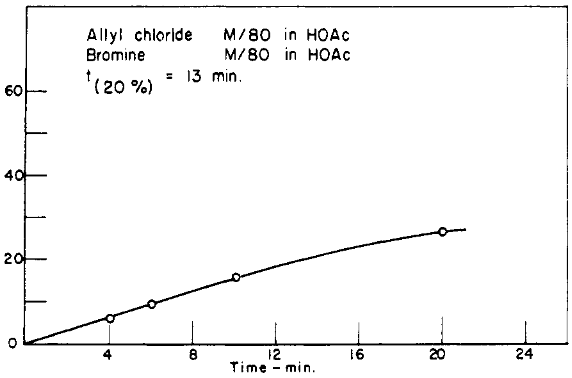

Fig. 1a. Bromine addition to allyl chloride

Procedure. The concentrations of the reactants are expressed as the concentration of the final solution. For example, for all bromine addition experiments, 5 ml. of the allylic chloride in glacial acetic acid (0.025*M*) and 5 ml. of bromine in glacial acetic acid (0.025*M*) were mixed in a 10-ml. colored volumetric flask to give a solution .0125*M* in each. For each time interval, 1 ml. of sample was taken out by a 1-ml. syringe (precision 0.001 ml.) and transferred into an iodine flask containing 10 ml. potassium iodide solution (5%). The solution was titrated with 0.01*N* sodium thiosulfate solution.

The values of X (% absorption of bromine) were plotted against time. From the resultant curves, as illustrated in Figure 1a, values of k_2 were calculated in (l.) (g.-mole)$^{-1}$ (min.)$^{-1}$. The results for the homogeneous reactions are reproducible.

B. *Addition of chlorine. Reagent.* Chlorine gas was dissolved in glacial acetic acid to prepare the solutions of required concentrations. Besides glacial acetic acid, three other aqueous acetic acid solutions were used: 10% water, 20% water and 40% water in acetic acid. Allyl chloride, 3,3-dichloropropene, and 3,3,3-trichloropropene were the same materials used for the bromine addition; 1,1,3-trichloropropene (b.p. 132°, 760 mm.), *cis*-1,3-dichloropropene (b.p. 104°, 760 mm.), *trans*-1,3-dichloropropene (b.p. 112°, 760 mm.), and vinyl bromide (b.p. 16°, 760 mm.) also were used in this experiment.

Procedure. Most of the procedure is identical with that of bromine addition, except that a special correction had to be made for the slight evaporation of chlorine.

The following sets of experiments were performed with different concentrations of acetic acid solutions. They could not be done at one concentration because of the great variation of rate. This procedure is valid provided a known value for one compound is available for each set of experimental conditions. Thus in Table II the relative rates for vinyl bromide and *cis*-dichloroethylene were known. The relative values obtained for *trans*-1,3-dichloropropene and 3,3,3-trichloropropene in the aqueous acetic acid with 20% water were in turn used as known values for comparisons made in solutions with 10% and 40% water in the acetic acid. It was found that the more dilute the acetic acid solution, the faster the rate for the less reactive allylic chlorides.

(a) In glacial acetic acid: (1) 3,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) Vinyl bromide (*M*/10), Chlorine (*M*/80).

(b) In aqueous acetic acid solution (10% water): (1) *cis*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) *trans*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80).

(c) In aqueous acetic acid solution (20% water): (1) *trans*-1,3-Dichloropropene (*M*/10), Chlorine (*M*/80). (2) 3,3,3-Trichloropropene (*M*/10), Chlorine (*M*/80).

(d) In aqueous acetic acid solution (40% water): (1) 3,3,3-Trichloropropene (*M*/10), Chlorine (*M*/80). (2) 1,1,3-Trichloropropene (*M*/10), Chlorine (*M*/80).

The values of X (% absorption of chlorine) were plotted against time as illustrated in Figure 1b and the rate k_2 evaluated from the slope (see Table I).

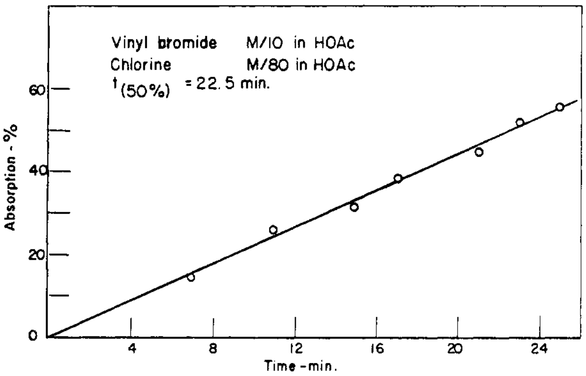

Fig. 1b. Chlorine addition to vinyl bromide

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On the Nitration of D-Fructose. I.

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Fructose was nitrated by nitronium sulfate. Six compounds were isolated, either as nitrate esters or—after denitration—as derivatives of fructose, four of which could be identified as dimeric condensation compounds of fructose anhydrides. Three of them are described: difructose-anhydride I, diheterolevulosan I, and diheterolevulosan II. A suggestion is put forward on the mechanism of their formation.

In their effort to identify possible decomposition products of cellulose nitrate[1] a large number of simple and compound sugars have been nitrated by Will and Lenze,[2] using nitronium sulfate as nitrating agent. Most of the sugars yielded the expected fully nitrated products, with the exception of xylose, glucose, fructose, and sucrose. From the monosaccharides crystalline nitrates of the anhydrides of the corresponding sugar could be obtained, besides some amorphous nitration products of ill-defined character. Complete nitration of xylose, glucose, and sucrose has been performed in more refined ways;[3-5] however, no success in full nitration of fructose has been reported.

This sugar differs from the others in its behavior towards strong mineral acids, the action of which causes dehydration and dimerization.[6] The properties of six difructose dianhydrides were summarized by Wolfrom *et al.*[7] The existence of monomeric

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