lization of 0.26 g. from acetone gave 0.22 g., m.p. 210–211°. A mixed melting point with the acetal obtained from the decomposition of *p*-nitrobenzyl nitrite gave no depression.

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Allylic Chlorides. XXV. The Reaction of 1,1,3-Trichloro-1-propene and 1,1-Dibromo-3-chloro-1-propene with Potassium Iodide in Acetone[1]

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The preparation and properties of 1,1,3-trichloro-1-propene and 1,1-dibromo-3-chloro-1-propene have been reported recently.[1] It was noted that the reaction of the 1,1-dihalo-3-chloro-1-propenes with potassium iodide, while giving the expected 1,1-dihalo-3-iodo-1-propenes, did not yield kinetic data of value at 20°.

Kinetic data have now been obtained for this reaction with 1,1,3-trichloro-1-propene at 0°, 5°, and 10° (Table I). From these data the energy of activation for the reaction was calculated by use of the Arrhenius equation to be 12 kcal./mole. The straight line relationship between $\ln k$ and $1/T$ indicated that k at 20° would be *ca.* 49. This figure represents a relative reactivity for 1,1,3-trichloro-1-propene of *ca.* 98 (allyl chloride as 1.00 with k = 0.502). When both 1,1-substituents are CH_3- the relative reactivity is 28.[2]

TABLE I

Reaction of 1,1,3-Trichloro-1-propene with Potassium Iodide in Acetone

Temper- . ature	Time, hr.	% Reacted	k hr.$^{-1}$ mole^{-1} l.	 Average
0.0°	0.50	59.2	9.64	
	0.63	67.2	9.56	
	0.78	74.0	9.50	
	0.87	76.8	9.36	
	1.08	82.7	9.07	9.42 ± 0.17
5.0°	0.25	51.5	15.6	
	0.37	65.2	15.6	
	0.47	73.3	15.4	
	0.57	79.1	15.3	
	0.62	80.9	14.8	15.3 ± 0.2
10.0°	0.16	48.5	21.3	
	0.28	67.1	21.3	
	0.35	74.2	21.5	
	0.44	81.4	21.3	
	0.50	83.8	20.4	21.2 ± 0.2

An attempt was made to obtain similar data for 1,1-dibromo-3-chloro-1-propene but the reaction was too fast at −10° to give acceptable kinetic data. Three points were obtained which gave an average k value of 151 ± 3.

The marked increase in reactivity in going from chlorine to bromine in the number 1 position has been noted previously[3] and ascribed to steric effects related to the size of the bromine atom. Apparently steric, inductive, and resonance effects all influence the reactivity of the allylic chlorine atom and this makes it difficult to relate cause and effect.[4]

EXPERIMENTAL

1,1,3-Trichloro-1-propene. 1,1,3-Trichloro-1-propane was prepared from 1,1-dichloro-1-propene by bromination using *N*-bromosuccinimide, hydrolysis of the 3-bromo-1,1-dichloro-1-propene to 3,3-dichloro-2-propen-1-ol and conversion of the alcohol to the trichloride using phosphorus trichloride in dry pyridine in a manner similar to that described previously.[1] B.p. 59° (50 mm.); n_D^{25} 1.4931 [lit.[1] b.p. 59.5° (50 mm.); n_D^{25} 1.4930].

1,1-Dibromo-3-chloro-1-propene. This compound was prepared from 1,1-dibromo-1-propene (0.25 mole) by reaction with *N*-chlorosuccinimide (0.25 mole) at 70° for 8 hr. in the presence of benzoyl peroxide (10 g.), using carbon tetrachloride as the solvent. A 47% yield of 1,1-dibromo-3-chloro-1-propene was obtained and it had the following physical constants: b.p. 37–38° (1.0 mm.); n_D^{25} 1.5620 [lit.[1] b.p. 35.5–36° (0.6 mm.); n_D^{25} 1.5634].

Reaction of 1,1,3-trichloro-1-propene with potassium iodide in acetone at 0°, 5° and 10°. The procedure used was similar to that described previously.[5] With the usual modified second-order rate equation, the plot of $\log 5\text{-}Z/(5)(1\text{-}Z)$ *vs.* time where Z is the fraction of potassium iodide having reacted in time t, gave a straight line between *ca.* 50 and 80% reacted at 0°, 5° and 10°. The rates at 0° and 5° showed some drift. The data are presented in Table I.

Reaction of 1,1-dibromo-3-chloro-1-propene with potassium iodide in acetone at −10°. Experimental difficulties prevented the obtaining of reliable kinetic data for this reaction. The following data are approximate.

Time, hr.	0.067	0.083	0.100
Reacted, %	85.	88.	93.
k, hr.$^{-1}$ mole^{-1} l.	159	146	149
Av. k		151 ± 3	

It is assumed that the vinyl bromine atoms have not reacted.[3]

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