

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

## Relative Reactivities of Organic Halides in Displacement Reactions. I. Allylic Chlorides

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Rates of reaction for a group of closely related allylic chlorides, both in the  $S_N2$  type reaction with potassium iodide in absolute acetone and in the  $S_N1$  type reaction with silver nitrate, are reported. The results are interpreted in terms of the structures of the allylic chlorides studied.

By earlier report<sup>1</sup> *n*-butylidene chloride is less reactive than *n*-butyl chloride both in  $S_N1$  reaction with silver nitrate in ethanol and in  $S_N2$  reaction with potassium iodide in acetone. In the benzyl chloride series, on the other hand, the  $S_N1$  reactivity clearly increases with an increase in the number of chlorine atoms on the  $\alpha$ -carbon, but the  $S_N2$  reactivity decreases. The lower  $S_N2$  reactivity of the polychlorides was ascribed to steric factors. Increase in  $S_N1$  reactivity in the series  $C_6H_5CH_2Cl < C_6H_5CHCl_2 < C_6H_5CCl_3$  was attributed to resonance stabilization of the carbonium ion through participation of the  $\alpha$ -chlorine atoms,<sup>2</sup> which in butylidene chloride appears to be outweighed by the electron withdrawing inductive effect of the chlorine atom in destabilizing the carbonium ion.

In the present work, the relative reactivities of allylidene chloride and other related allylic chlorides in both  $S_N1$  and  $S_N2$  type reactions were investigated. The results, together with related data of other workers, are shown in Tables I and II.

TABLE I  
RATES OF REACTION WITH POTASSIUM IODIDE IN ABSOLUTE ACETONE

Compound	Temp., °C.	$k$ , l. mole <sup>-1</sup> hr. <sup>-1</sup>
Allyl chloride	20	0.218 <sup>a</sup>
Allylidene chloride	25	.003
	50	.07
<i>trans</i> -1,3-Dichloro-1-propene	20	.632 <sup>a</sup>
<i>cis</i> -1,3-Dichloro-1-propene	20	1.87 <sup>a</sup>
Crotyl chloride	20	0.535 <sup>b</sup>
Methylvinylcarbinyl chloride	20	.005
	50	.111

<sup>a</sup> L. F. Hatch, L. B. Gordon and J. J. Russ, *THIS JOURNAL*, **70**, 1093 (1948). <sup>b</sup> M. Tamele, C. J. Ott, K. E. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

TABLE II  
RATES OF REACTION WITH SILVER NITRATE IN ABSOLUTE ETHANOL

Compound	Temp., °C.	$10^4 k$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
Allyl chloride	25	0.173
	50	1.74
Allylidene chloride	50	4.22
<i>trans</i> -1,3-Dichloro-1-propene	50	4.31
<i>cis</i> -1,3-Dichloro-1-propene	50	2.48
Crotyl chloride	25	55.6
Methylvinylcarbinyl chloride	25	32.5

### Experimental

**Materials.**—Commercial absolute ethanol was refluxed over calcium oxide for several hours and then distilled.

(1) M. Murakami, S. Oae and S. Takeuchi, *Bull. Chem. Soc. Japan*, **24**, 1 (1951).

(2) See J. Hine and D. E. Lee, *THIS JOURNAL*, **73**, 22 (1951).

The distilled product was refluxed over silver nitrate in order to remove any aldehyde and was then distilled through an efficient column, the fraction distilling at 77.9° (741 mm.) being collected.

Mallinckrodt analytical reagent silver nitrate was used directly. Solutions were stored in the dark and were freshly prepared at least once a week.

Acetone was refluxed over potassium permanganate for several hours and distilled. The distillate was dried over Drierite for three days, the fraction distilling at 56.2° (734 mm.) being collected.

Mallinckrodt analytical reagent potassium iodide and Baker and Adamson analytical reagent potassium iodate were used directly.

Commercial allyl chloride was washed first with concentrated hydrochloric acid, then with sodium carbonate solution, dried over calcium chloride, and distilled through an efficient column. The fraction distilling at 44.8–45° (729 mm.) was collected.

Allylidene chloride was prepared by dropping 70 g. of freshly distilled acrolein onto 210 g. of phosphorus pentachloride at 0° over the course of 90 minutes. The reaction mixture was allowed to stand for 14 hours. Then the upper layer was separated and washed several times with 10% sodium bicarbonate solution and with water and then dried over calcium chloride. The dried product was fractionated through an efficient glass helices-packed column, the fraction boiling at 83–85° (728 mm.) being collected. This was refractionated: the 25-g. portion boiling at 84–84.5° (728 mm.) was collected.

A mixture of *cis*- and *trans*-1,3-dichloro-1-propene<sup>3</sup> was fractionated through an efficient glass helices-packed column. The fractions distilling at 104 and 111° at 730 mm. were collected separately, washed with 10% sodium bicarbonate solution and dried over calcium chloride. Each fraction was then refractionated. The lower boiling isomer,  $n_D^{20}$  1.4675, has been assigned the *cis*-configuration and the higher boiling isomer,  $n_D^{20}$  1.4740, the *trans*-configuration.<sup>4</sup>

Crotyl chloride and methylvinylcarbinyl chloride were prepared by mixing of 72 g. of crotyl alcohol and 250 ml. of concentrated hydrochloric acid in a separatory funnel. After a shaking period of one hour, the upper layer was separated, washed with 10% sodium bicarbonate solution and dried over calcium chloride. The well-dried oil was fractionated through an efficient column, the fractions boiling at 60–65° and 80–83° at 730 mm. being collected. Refractionation of the lower-boiling fraction yielded 30 g. of methylvinylcarbinyl chloride, b.p. 63.0° (730 mm.),  $n_D^{20}$  1.4151; of the higher-boiling fraction, 40 g. of crotyl chloride, b.p. 82° (730 mm.),  $n_D^{20}$  1.4343.

**Determination of Rate Constants.**—Rate constants for the reactions of the chlorides with potassium iodide in absolute acetone were determined by the standard method.<sup>5</sup>

The method used for the determination of the rate constants for the reactions with silver nitrate was similar to that employed by Burke and Donnan<sup>6</sup> and Senter,<sup>7</sup> except that all runs were carried out in a dark room in order to prevent the catalytic action of silver chloride formed during the reaction. A mixture of 5 ml. each of a 1 *N* ethanol solution of the organic halide and a 2 *N* ethanol solution of silver nitrate was sealed in a 20-ml. ampoule and immediately im-

(3) Obtained through the kindness of the Shell Oil Company, N. J.

(4) L. F. Hatch and P. H. Perry, Jr., *THIS JOURNAL*, **71**, 3262 (1949).

(5) (a) Ref. (a), Table I; (b) Ref. (b), Table I; (c) J. B. Conant and W. R. Kirner, *THIS JOURNAL*, **46**, 232 (1924); J. B. Conant and R. E. Hussey, *ibid.*, **47**, 476 (1925).

(6) K. A. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

(7) G. Senter, *ibid.*, **97**, 346 (1910).

mersed in a thermostat. At regular intervals, the ampoules were broken and the contents washed into 25 ml. of a 0.5 *N* solution of ammonium thiocyanate; the resulting solution was back titrated with 0.05 *N* silver nitrate in the presence of iron alum indicator. The rate constant for each point was calculated from the second-order equation

$$k = \frac{2.303}{0.05t} \log \frac{b(a-x)}{a(b-x)}$$

The values reported represent the means of several individual runs.

The products formed from the reaction of silver nitrate with allylidene chloride and with *trans*-1,3-dichloro-1-propene, respectively, were investigated and found to be identical.

**Isolation of Product in Reaction of Silver Nitrate with *trans*-1,3-Dichloro-1-propene and with Allylidene Chloride.**—Exactly 22.9 g. of freshly distilled *trans*-1,3-dichloro-1-propene (or the same amount of freshly distilled allylidene chloride) was added to a solution of 35 g. of silver nitrate in 1 l. of absolute alcohol. The resulting mixture was then heated at the reflux temperature for one hour. The precipitated silver chloride was removed by filtration, and the filtrate was fractionated through an efficient distilling column to yield 16 g. (17 g. in the case of the allylidene chloride) of product, presumably 3-chloro-2-propenyl nitrate, b.p. 87° (50 mm.),  $n_D^{25}$  1.4519 (1.4518 for product from allylidene chloride).

*Anal.* Calcd. for C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>NCl: N, 10.2; Cl, 25.8. Found: N, 10.1; Cl, 25.9. (For product from allylidene chloride: N, 9.9; Cl, 26.1.)

### Discussion

The lower reactivity of allylidene chloride, compared with allyl chloride or with the 1,3-dichloro-1-propenes, in S<sub>N</sub>2 reaction with potassium iodide in acetone, can best be explained on the basis of steric factors. The order of reactivity of allylidene chloride is, in fact, quite similar to that of the secondary halide methylvinylcarbinyl chloride. Allylidene chloride is known to react slowly with other nucleophilic reagents such as sodium ethoxide,<sup>8</sup> sodium hydroxide,<sup>9</sup> sodium acetate,<sup>8b</sup> phenylmagnesium bromide<sup>8b</sup> and diethylamine.<sup>8b</sup>

The increased reactivity of crotyl chloride over that of allyl chloride in S<sub>N</sub>2 reaction is unexpected. The fact that *cis*-1,3-dichloro-1-propene reacts approximately four times as fast as the *trans* isomer is also difficult to explain. It has been reported<sup>10,8a</sup> that with sodium ethoxide the

*trans* isomer is the more reactive. The suggestion<sup>10</sup> that the reactions with potassium iodide and sodium ethoxide proceed *via* different mechanisms does not seem plausible in view of the established S<sub>N</sub>2 nature of the potassium iodide reaction<sup>11</sup> and the fact that the reaction with sodium ethoxide gives only the normal substitution product, 1-chloro-3-ethoxy-1-propene.<sup>8a</sup>

The increased reactivity of allylidene chloride over that of allyl chloride in the S<sub>N</sub>1 type reaction with silver nitrate parallels the benzal chloride > benzyl chloride sequence and may be attributed to resonance stabilization of the carbonium ion intermediate through participation of the chlorine. It is noteworthy that allylidene chloride and *trans*-1,3-dichloro-1-propene show almost identical reaction rates and give the same products, indicating that the reactions with the two halides proceed *via* a common intermediate.

We can offer no satisfactory explanation for the observed differences in the rates of reaction of *cis*- and of *trans*-1,3-dichloro-1-propene and of allylidene chloride, although for the isomeric 1,3-dichloro-1-propenes the rates vary in the same order as those reported<sup>12</sup> for the cuprous chloride-catalyzed hydrolysis of the chlorides.

The increased reactivity of crotyl chloride over that of allyl chloride may reasonably be attributed to the hyperconjugative stabilization of the intermediate carbonium ion by the methyl group. On the other hand, the fact that crotyl chloride reacts more rapidly with silver nitrate than does methylvinylcarbinyl chloride is surprising. A similar anomaly was observed in the hydrolysis of these chlorides by Young and Andrews,<sup>11</sup> who suggested that the observed first-order reaction of the primary chloride might be in part a bimolecular reaction with solvent giving rise to the normal product in an ordinary S<sub>N</sub>2 reaction. Such a possibility does not appear probable in the reaction with silver nitrate, although it is possible that the primary chloride has a more favorable structure for solvolysis in a concerted mechanism type reaction.

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LAWRENCE, KANSAS

(8) (a) H. A. Smith and W. H. King, *THIS JOURNAL*, **73**, 95 (1950);

(b) A. Kirrmann, Pacaud and H. Dosque, *Bull. soc. chim.*, [5] **1**, 860 (1934).

(9) L. J. Andrews and R. E. Keefer, *THIS JOURNAL*, **70**, 3456 (1948).

(10) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

(11) W. G. Young and L. J. Andrews, *ibid.*, **66**, 421 (1944).

(12) L. F. Hatch, A. N. Brown and H. P. Bailey, *ibid.*, **72**, 3198 (1950).