single peak with a retention time identical with that of the *minor* component from the mixture of epimeric esters prepared according to the method of Wiberg.[6]

The nuclear magnetic resonance spectrum of this ester had a sharp three-proton singlet at τ 6.37 (OCH_3), a partially resolved doublet at 7.27 ($J = 2.5$ c.p.s.), accounting for two bridgehead protons, a broad one-proton doublet centered at *ca.* 7.8 (*exo* C-6 hydrogen) which is partially obscured by a sharp one-proton doublet at 7.88 ($J = 7.5$ c.p.s., *endo* C-5 hydrogen). A four-proton singlet at τ 8.62 (C-2 and C-3 hydrogens) and a one-proton triplet centered at 9.00 ($J = 7.5$ c.p.s.) for the *endo* C-6 hydrogen complete the spectrum.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.76.

Isomerizations of 1-Chloro-2-butene and 3-Chloro-1-butene[1]

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The average equilibrium constant for the isomerization of 3-chloro-1-butene to 1-chloro-2-butene in toluene at 80.2° was 2.32. The isomerization was catalyzed by Pyrex glass wool and by diethylamine hydrochloride. The kinetics of the isomerization was pseudo zero order, and the ratio of the rate constants for the forward and reverse reactions gave the same value (within experimental error) of the equilibrium constant as that determined from the composition of butenyl chlorides at equilibrium. The isomerization may be interpreted as occurring by way of ion pairs produced on the surface of electrophilic catalysts. Isomerization is inhibited if the butenyl chloride is stored at 0° in quartz flasks.

The rearrangement of allylic compounds is well known and may occur by way of a displacement reaction (S_N2′)[4] or by ionization to ion pairs.[5]

Young and Winstein had shown that an equilibrium mixture of 3-bromo-1-butene and 1-bromo-2-butene (neat) at 100° consisted of about 15% of the former and 85% of the latter.[6] Lewis acids were found to catalyze the interconversion of 3-chloro-1-butene and 1-chloro-2-butene,[7a,b] and the equilibrium mixture at 60° was reported to consist of 26% of the former and 74% of the latter when cuprous chloride was the catalyst.[7b]

In studies on the SN2′ reaction of amines with 3-chloro-1-butene it was shown that the latter did not isomerize significantly under the conditions of the reaction.[8] At late stages of the relatively slow reaction of 3-chloro-1-butene with N-methylaniline some isomerization of the chloride could be detected by gas chromatography.[9] In the reaction of 3-chloro-3-phenyl-1-butene with triethylamine or with dimethylamine, isomerization of the halide was an important complication.[10]

The purpose of our investigation was to determine the rates of isomerization of 1-chloro-2-butene and 3-chloro-1-butene and the conditions under which isomerization may be a complicating factor in SN2′ reactions especially with relatively unreactive amines such as N-methylaniline.

Results

The equilibrium constant (based on concentrations) for the isomerization of 3-chloro-1-butene to 1-chloro-2-butene in toluene at 80.2° was obtained by gas chromatographic determination of the concentrations of the two isomers at equilibrium. The constant, K, obtained in this way had values ranging from 2.19 to 2.34. The equilibrium constant was determined also by the ratio of rate constants for the forward and reverse reactions. The rate of isomerization was catalyzed by diethylamine hydrochloride and by Pyrex glass wool and the rate actually observed was zero order, independent of the concentration of allylic chloride. A derivation of the pseudo zero order kinetics based on a surface-catalyzed isomerization is given in the Experimental section. Isomerization of 1-chloro-2-butene occurs readily when it is stored in a glass vessel; the isomerization is inhibited when it is stored in a quartz flask at 0°.

$$\mathrm{CH_2{=}CHCH(CH_3)Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3CH{=}CHCH_2Cl}$$

$$K = k_1/k_{-1}$$

TABLE I

COMPOSITION OF EQUILIBRIUM MIXTURE OF 1.113 *M* 3-CHLORO-1-BUTENE AND 1.113 *M* 1-CHLORO-2-BUTENE IN TOLUENE AT 80.2°

Time, hr.	3-Chloro-1-butene, mole %	1-Chloro-2-butene, mole %	K
0	100.0	0.0	. . .
3137	30.3	69.7	2.30[a]
3884	31.3	68.7	2.19[a]
0	0.0	100.0	. . .
3465	31.2	68.8	2.21[a]
4238	29.9	70.1	2.34[a]
0	100.0	0.0	. . .
3573	29.8	70.2	2.36[b]
3978	30.1	69.9	2.33[b]
0	0.0	100.0	. . .
2325	30.9	69.1	2.24[b]
3067	29.0	71.0	2.45[b]

[a] $(C_2H_5)_2NH_2Cl$ (0.1 g.) added/5 ml. of solution. [b] $(C_2H_5)_2NH_2Cl$ (0.1 g.) and Pyrex glass wool (0.4 g.) added/5 ml. of solution.

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[1] For experimental details, see A. F. Marcantonio, Ph.D. Thesis, University of Pennsylvania, 1961.

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[5] E. A. Braude, *Quart. Rev.*, **4**, 419 (1950); W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951); R. A. Sneen and A. M. Rosenberg, *ibid.*, **83**, 900 (1961); H. L. Goering, J. P. Blanchard, and E. F. Silversmith, *ibid.*, **76**, 5409 (1954).

[6] S. Winstein and W. G. Young, *ibid.*, **58**, 104 (1936).

[7] (a) M. S. Kharasch, J. Kritchevesky, and F. R. Mayo, *J. Org. Chem.*, **2**, 489 (1937); D. P. Young, British Patent 798,889 (1958); *Chem. Abstr.*, **53**, 6077 (1959); (b) J. F. Lane, J. Fentress, and L. T. Sherwood, Jr., *J. Am. Chem. Soc.*, **66**, 545 (1944).

[8] W. G. Young, I. D. Webb, and H. L. Goering, *ibid.*, **73**, 1076 (1951).

[9] D. C. Dittmer and A. F. Marcantonio, *ibid.*, in press.

[10] G. Valkanas and E. S. Waight, *J. Chem. Soc.*, 531 (1964).

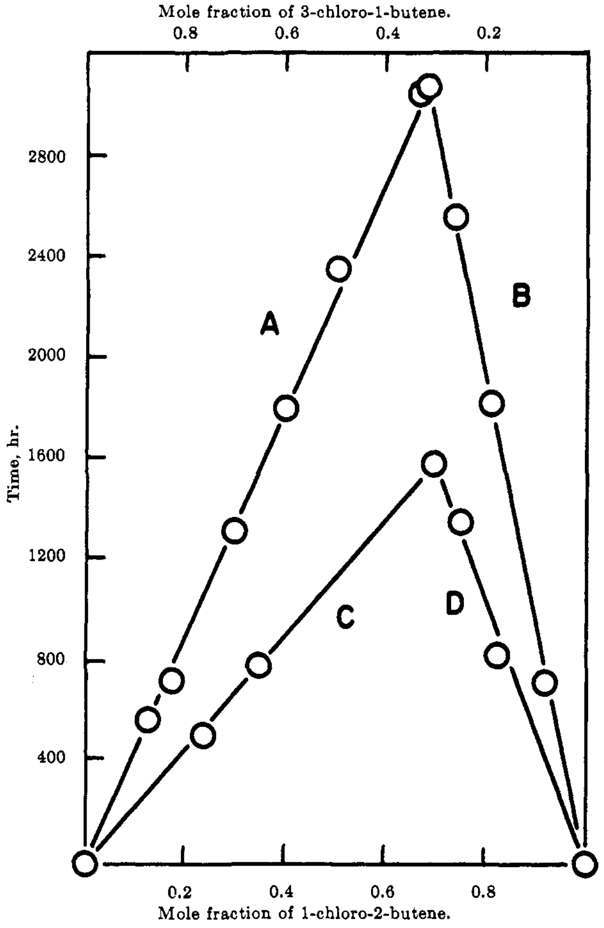


Fig. 1.—Zero-order rate plot for the heterogeneous catalysis of isomerization of butenyl allylic chlorides. The isomerization of 1.113 *M* 3-chloro-1-butene to 1-chloro-2-butene (A) and 1.113 *M* 1-chloro-2-butene to 3-chloro-1-butene (B) in toluene in the presence of 0.1 g. of diethylamine hydrochloride/5 ml. of solution at 80.2 ± 0.1°; and the isomerization of 1.113 *M* 3-chloro-1-butene to 1-chloro-2-butene (C) and 1.113 *M* 1-chloro-2-butene to 3-chloro-1-butene (D) in toluene in the presence of 0.1 g. of diethylamine hydrochloride and 0.4 g. of Pyrex glass wool/5 ml. of solution at 80.2 ± 0.1°.

Table I shows values of the equilibrium constant obtained from concentrations at equilibrium, and Table II shows the values of the equilibrium constant obtained from rate constants. Figure 1 illustrates the isomerization and shows the effect of glass wool on the rate.

TABLE II

RATE AND EQUILIBRIUM CONSTANTS FOR ISOMERIZATION OF BUTENYL ALLYLIC CHLORIDES IN TOLUENE AT 80.2°

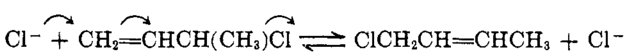
Concentration of reactant, *M*	$10^5k_1{}^a$	$10^5k_{-1}{}^a$	$K = k_1/k_{-1}$
2.0 Butenyl chloride	15.7	6.59	2.38
1.1 Butenyl chloride[b]	22.0	9.52	2.31
1.1 Butenyl chloride[c]	45.5	19.2	2.37
2.0 Butenyl chloride[b]	23.4	10.0	2.34

[a] Pseudo-zero-order rate constants in mole fractions/hr. [b] $(C_2H_5)_2NH_2Cl$ (0.1 g.)/5 ml. of solution. [c] $(C_2H_5)_2NH_2Cl$ (0.1 g.)/5 ml. of solution + Pyrex glass wool (0.4 g.)/5 ml. of solution.

It was not possible to determine the *cis–trans* ratio of the 1-chloro-2-butene in the reaction mixture.

Discussion

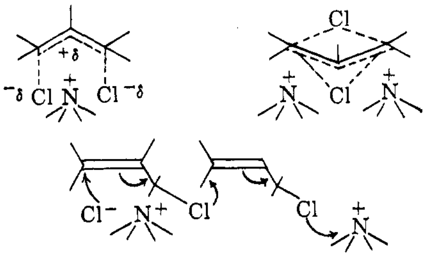
Isomerization may occur *via* attack of a small amount of chloride ion on the double bond with rearrangement of the double bond.



$$Cl^- + CH_2{=}CHCH(CH_3)Cl \rightleftharpoons ClCH_2CH{=}CHCH_3 + Cl^-$$

If the concentration of chloride ions was very small relative to the concentration of allylic halide, the over-all kinetics would appear to be zero order. However, isomerization occurs in the absence of added diethylamine hydrochloride; no induction period was observed pending the production of hydrogen chloride in a side reaction such as formation of butadiene. No evidence could be obtained by gas chromatography for the formation of butadiene.

The zero-order kinetics suggests a heterogeneous reaction on a surface which is saturated with reactant.[11] The catalytic effect of the amine hydrochloride or of the Pyrex glass wool may involve an isomerization at the surface of the solid phase. The following schemes in which intimate ion pairs[12] are involved may account for the isomerization catalyzed by amine hydrochloride. The first of these is analogous to the scheme proposed for the isomerization of 3-phenyl-3-chloro-1-butene by lithium chloride.[13] Other schemes in which the acidic proton of the amine hydrochloride assists isomerization by hydrogen bonding to chlorine are possible also.



Pyrex glass contains a considerable amount of boric oxide (B_2O_3), the boron atoms of which may aid in electrophilic solvation of the chloride ion. The isomerization on the glass surface may be pictured similarly to the above schemes with the substitution of boron for the positively charged nitrogen. The N–H proton in N-methylaniline has been suggested as being involved in solvating leaving chloride ion by hydrogen bonding.[9]

If the isomerization is assumed to be essentially unimolecular at the catalyst surface and if the surface is assumed to be nearly completely covered, it can be shown (see Experimental section) that the kinetics would be pseudo zero order.

The greater proportion of 1-chloro-2-butene at equilibrium indicates its greater thermodynamic stability; from the equilibrium constant at 80.2° a ΔF of about −0.6 kcal./mole can be calculated. This difference in free energies is less than the difference in gas-phase free energies of formation at 25° between 1-butene and either *cis-* or *trans*-2-butene (1.2 and 1.9 kcal./mole, respectively).[14] It is not strictly fair to compare gas-phase values of free energy at one temperature with liquid (solution) phase values at another temperature, but it is likely that effects caused by the temperature

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[11] G.-M. Schwab, H. S. Taylor, and R. W. Spence, "Catalysis," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 223.

[12] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (London), 664 (1954).

[13] G. Valkanas and E. S. Waight, *J. Chem. Soc.*, 2720 (1959).

[14] "Tables of Selected Properties of Hydrocarbons," American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C., Table 8p, part 1.

difference and by heats and entropies of condensation and solution are largely cancelled in the comparisons between the butenyl chlorides and the butenes. The largest differences in free energies between isomers are most likely to be found in the free energies of formation.

A Stuart–Briegleb model of 1-chloro-2-butene shows steric hindrance between the chlorine atom and a *cis* olefinic hydrogen or *cis* methyl group which would increase the free energy and thus decrease the free energy difference between 1-chloro-2-butene and 3-chloro-1-butene relative to the difference between 1- and 2-butene. Models indicate no large steric differences between 3-chloro-1-butene and 1-butene.

Experimental

The butenyl chlorides were prepared and analyzed by gas chromatography as described previously.[9] There was no evidence for isomerization of the pure butenyl chlorides on a Carbowax 20 M column at 100°. *cis* and *trans* isomers were not separated.

Pyrex glass wool was immersed for 48 hr. in a solution of equal quantities of concentrated hydrochloric acid and distilled water. The glass wool was washed thoroughly with distilled water until the washings were free from chloride ion as determined by aqueous silver nitrate. It was dried in an oven at 110° overnight and stored while still hot in a desiccator.

Kinetic Procedure.—Aliquots (5 ml.) of stock solutions of either 3-chloro-1-butene or 1-chloro-3-butene in dry toluene[15] were pipetted into Pyrex test tubes containing catalyst as required. The tubes were sealed and placed in a constant-temperature bath, the contents of one tube being analyzed at once to give a zero-time point. At various times a tube was removed from the bath and the reaction was quenched by immersing the tube in a dry acetone bath.[16] The contents of the tube were poured into a quartz erlenmeyer flask and stoppered until the contents could be analyzed by gas chromatography. 1-Chloro-2-butene can be stored in a quartz flask at 0° for long periods of time without the isomerization which occurs on storage in glass flasks.

Derivation of Observed Kinetics.—This derivation makes use of the theory of Langmuir for the adsorption of substances on surfaces.[17]

Assume two isomers A and B which are adsorbed (ads) on a surface and are interconverted on a surface.

$$\mathrm{A} \rightleftharpoons \mathrm{A_{ads}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B_{ads}} \rightleftharpoons \mathrm{B}$$

The following definitions are made.

μ_A = moles of A striking 1 cm.^{2} of surface/sec. $\sim$[A]
μ_B = moles of B striking 1 cm.^{2} of surface/sec. $\sim$[B]
α_A = fraction of moles of A which stick on surface
α_B = fraction of moles of B which stick on surface
θ_A = fraction of surface covered by A at any time $\sim A_{ads}$
θ_B = fraction of surface covered by B at any time $\sim B_{ads}$
$1 - \theta_A - \theta_B$ = fraction of surface that is bare
$(1 - \theta_A - \theta_B)\alpha_A\mu_A$ = rate adsorption of A on surface
$(1 - \theta_A - \theta_B)\alpha_B\mu_B$ = rate adsorption of B on surface
$\omega_A\theta_A$ = rate desorption of A
$\omega_B\theta_B$ = rate desorption of B where ω_A, ω_B are constants

The rate of formation of A_{ads} is given by

$$\frac{d[\mathrm{A_{ads}}]}{dt} \cong \frac{d\theta_A}{dt} = (1 - \theta_A - \theta_B)\alpha_A\mu_A - \omega_A\theta_A - k_1[\mathrm{A_{ads}}] + k_{-1}[\mathrm{B}]_{ads} = (1 - \theta_A - \theta_B)\alpha_A\mu_A - \omega_A\theta_A - k_1'\theta_A + k_{-1}'\theta_B$$

where $k_1' = k_1$ times a constant and $k_{-1}' = k_{-1}$ times a constant; the proportionality constant between θ_A and A_{ads} and θ_B and B_{ads} is assumed the same.

If the surface is assumed to be nearly completely covered

$$1 \cong \theta_A + \theta_B$$

$$\frac{d\theta_A}{dt} = -\omega_A\theta_A - k_1'\theta_A + k_{-1}' - k_{-1}'\theta_A = k_{-1}' - \theta_A(\omega_A + k_1' + k_{-1}')$$

Let $(\omega_A + k_1' + k_{-1}') = b$

$$\frac{d(\theta_A)}{dt} = k_{-1}' - b\theta_A$$

$$\int_0^t dt = \int_{\theta_A = 0}^{\theta_A} \frac{d\theta_A}{k_{-1}' - b\theta_A}$$

(If one starts with pure B, at $t = 0$, $\theta_A = 0$.)

$$\ln\left(\frac{k_{-1}' - b\theta_A}{k_{-1}'}\right) = -bt$$

$$\ln\left(1 - \frac{b}{k_{-1}'}, \theta_A\right) = -bt$$

Let $-\frac{b}{k_{-1}'}, = c$

$$\ln(1 + c\theta_A) = -bt$$

Assume that $-1 < c\theta_A < 1$

$$\ln(1 + c\theta_A) = c\theta_A - \frac{1}{2}(c\theta_A)^2 + \frac{1}{3}(c\theta_A)^3 + \ldots$$

Assume $c\theta_A \gg (c\theta_A)^2 \gg (c\theta_A)^3$ etc.

Therefore

$$\ln(1 + c\theta_A) \cong c\theta_A$$

$$c\theta_A = -bt$$

$$\frac{\theta_A}{t} = -\frac{b}{c} = k_{-1}'$$

$$\frac{A_{ads}}{t} = k_{-1}$$

Since $A_{ads} \sim$ A

$$\frac{A}{t} \sim k_{-1}$$

The same treatment applied to a reaction in which pure A is isomerized yields

$$\frac{[\mathrm{B}]}{t} \sim k_1$$

The equilibrium constant is

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]_{ads}}{[\mathrm{A}]_{ads}} \cong \frac{[\mathrm{B}]}{[\mathrm{A}]}$$

This derivation shows that the rate constants obtained by dividing the concentration of reactant by time are pseudo-zero-order rate constants most probably because of the nearly complete absorption on a catalyst surface. The assumptions are not justifiable except that they lead to the experimental findings.

Acknowledgment.—We wish to thank Dr. Erwin Fishman for helpful discussions.

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[15] These solutions were free of hydrogen chloride as indicated by the lack of chloride ion in aqueous extracts of these stock solutions.

[16] No butadiene could be detected when samples of the mixture opened and kept at Dry Ice–acetone temperatures were injected into the gas chromatograph.

[17] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2267 (1916).