Friedel–Crafts Isomerization. XVI.[1a] Aluminum Chloride Catalyzed Isomerization of Cyclopropylcarbinyl and Cyclobutyl Chlorides

George A. Olah and Chi-Hsiung Lin[1b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received May 13, 1968

Abstract: Kinetic studies of the aluminum chloride catalyzed isomerization of cyclopropylcarbinyl chloride and cyclobutyl chloride showed no tendency to form any equilibrium mixture. The final product is always exclusively allylcarbinyl chloride. Mechanisms of these isomerizations were elucidated by kinetic data in nitromethane–chlorobenzene mixed solvent system. At −40 to −20° cyclopropylcarbinyl chloride rearranges to cyclobutyl chloride and allylcarbinyl chloride through a suggested SN2′ mechanism while cyclobutyl chloride rearranges to allylcarbinyl chloride through both SN2′ and SN1′ mechanisms, preferably the latter in more polar media. The rearrangement of cyclobutyl chloride to cyclopropylcarbinyl chloride was observed only at temperatures above +15°. No formation of cyclopropylcarbinyl or cyclobutyl chloride from allylcarbinyl chloride was observed under the reaction conditions. Arrhenius plots showed activation energies of 18.7 and 20.4 kcal for the rearrangement of cyclopropylcarbinyl chloride to cyclobutyl chloride and to allylcarbinyl chloride, respectively, and 27.3 kcal for that of cyclobutyl chloride to allylcarbinyl chloride. An estimated value of 45 kcal of activation energy was derived for the rearrangement of cyclobutyl chloride to cyclopropylcarbinyl chloride. Second-order kinetics in the concentration of these three chlorides was also obtained for their polymerization reaction. The relative rate constants are $1:6 \times 10^6:4.5 \times 10^{-3}$ for cyclopropylcarbinyl–cyclobutyl–allylcarbinyl chlorides at 40°.

Numerous investigations have been focused on the unusual reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives which frequently result in mixed products of all three systems.[2] The original isotope scrambling investigation by Roberts, *et al.*, in the rearrangement of cyclopropylcarbinol-α-^{14}C by Lucas reagent[3] provided the strongest evidence that the rearrangement proceeds through a carbonium ion intermediate. They also demonstrated that the rearrangement cannot be of an intramolecular type.[4] These findings and subsequent investigations by many other authors on the reactivity of compounds with α-cyclopropyl groups have built up the tendency to consider all reactions of such compounds to be of a carbonium ion type mechanism. The special stabilization effect of the α-cyclopropyl group on the carbonium ion is thus discussed and established. A study on the mutual rearrangement of cyclopropylcarbinyl chloride and cyclobutyl chloride by zinc chloride was reported by Roberts, *et al.*[5] The purpose of the present work is to study the mechanism of the aluminum chloride catalyzed rearrangement of cyclopropylcarbinyl and cyclobutyl chlorides and to see whether the reactions actually go through a carbonium ion type intermediate whose nature is of current interest.

Results

Kinetics. The especially high reactivity of cyclopropylcarbinyl and cyclobutyl chlorides prevents the possibility of a kinetic study of the rearrangement of the neat halides by aluminum chloride as is generally done in the study of alkyl halide rearrangements.[6] Even at −70°, the reaction proceeds explosively as soon as part of the aluminum chloride is dissolved into the chlorides. This exothermic reaction results in a dark brown solution in which allylcarbinyl chloride is the main low molecular weight component. To mollify the reaction, it was necessary to dilute the chloride with an inert solvent or to complex the Lewis acid beforehand.

Aluminum chloride and nitromethane form a very stable 1:1 complex which is easily crystallized at room temperature.[7] This complex formation is the reason for the decrease of activity of aluminum chloride in nitromethane solution as the reagent in Friedel–Crafts and related reactions[8] since the free energy of the initial system is lowered by the extent comparable to the bond energy of the O–Al bond in the complex. The amount of internal energy lowering, ΔE^0, decides the following equilibrium where RCl is the starting chloride in the reaction

$$\mathrm{RCl} + \mathrm{CH_3NO_2AlCl_3} \rightleftharpoons \mathrm{RCl\text{-}AlCl_3} + \mathrm{CH_3NO_2}$$

$$K = \frac{[\mathrm{RCl\text{-}AlCl_3}][\mathrm{CH_3NO_2}]}{[\mathrm{RCl}][\mathrm{CH_3NO_2\text{-}AlCl_3}]} = C\exp(-\Delta E^0/RT) \qquad (1)$$

If this equilibrium is sufficiently faster than the subsequent Friedel–Crafts type of reaction, as generally is the case when large amounts of aluminum chloride and nitromethane exist in the system, then the rate expression for the general reaction

$$\mathrm{RCl\text{-}AlCl_3} + \mathrm{B} + \ldots \longrightarrow \text{products}$$

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(1) (a) Part XV: G. A. Olah and J. A. Olah, *J. Org. Chem.*, **32**, 1612 (1967); (b) taken in part from the Ph.D. thesis of C. H. Lin, Case Western Reserve University, 1968.

(2) For a detailed review, see M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967), and literature suggested therein.

(3) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959).

(4) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(5) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(6) G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 729, 733 (1963); P. J. Trotter, *J. Org. Chem.*, **28**, 2093 (1963); R. Maurel and M. Bechet, *C. R. Acad. Sci., Paris*, **255**, 671 (1962).

(7) P. Gagnaux and B. P. Susz, *Helv. Chim. Acta*, **44**, 1128, 1132 (1961); J. Reichel and R. Vilceanu, *Bul. Stiint. Tehnic Inst. Politehnic Timisoara*, **10**, 71 (1965); *Chem. Abstr.*, **66**, 70439 (1967).

(8) G. A. Olah, "Friedel–Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y., 1964; I. Reichel and R. Vilceanu, *Rev. Chim.* (Bucharest), **11**, 206 (1960).

becomes

$$\text{rate} = -\frac{d[\text{RCl-AlCl}_3]}{dt} = -\frac{d[\text{RCl}]}{dt}$$
$$= A_0 \exp(-\Delta E_{a0}/RT)[\text{RCl-AlCl}_3][\text{B}]\ldots$$
$$= A \exp(-\Delta E_a/RT)\frac{[\text{CH}_3\text{NO}_2\text{-AlCl}_3]}{[\text{CH}_3\text{NO}_2]}[\text{RCl}][\text{B}]\ldots \quad (2)$$

where the frequency factor A is the product of A_0 and C, and the Arrhenius activation energy ΔE_a is the sum of ΔE_{a0} and ΔE^0. This means that the initial state referred to in rate expression 2 is $RCl + CH_3NO_2\text{-}AlCl_3$. The same is also true when the rate constant expression of the absolute rate theory is adopted as

$$\text{rate} = \frac{kT}{h}\exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right)\frac{[\text{CH}_3\text{NO}_2\text{-AlCl}_3]}{[\text{CH}_3\text{NO}_2]}[\text{RCl}][\text{B}]\ldots \quad (3)$$

where the entropy of activation, $\Delta S^{\ddagger}$, and the enthalpy of activation, $\Delta H^{\ddagger}$, are similarly based on the above specified initial state.

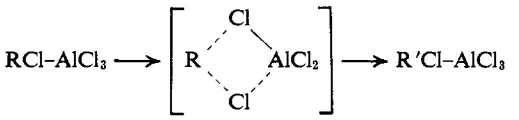
Assuming the conversion of aluminum chloride to the complex in nitromethane solution is complete, it is quite easy to prepare a solution for any predetermined ratio of $[CH_3NO_2\text{-}AlCl_3]/[CH_3NO_2]$. Let this ratio be represented by r. The rate expression for the consumption of RCl then becomes

$$-\frac{d[\text{RCl}]}{dt} = k_{\text{exptl}}[\text{RCl}][\text{B}]\ldots$$
$$= A \exp(-\Delta E_a/RT)r[\text{RCl}][\text{B}]\ldots \quad (2')$$
$$= (kT/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)r[\text{RCl}][\text{B}]\ldots \quad (3')$$

In the isomerization of chlorides, the concentration of $CH_3NO_2\text{-}AlCl_3$ remains constant, so the value r is a constant throughout the reaction.

For a unimolecular rearrangement by either an SN1′ or SNi′ mechanism, given respectively

$$\text{RCl-AlCl}_3 \underset{\text{fast}}{\xrightarrow{\text{slow}}} \text{R}^+\text{AlCl}_4^- \underset{\text{slow}}{\xrightarrow{\text{fast}}} \text{R}'^+\text{AlCl}_4^- \underset{\text{fast}}{\xrightarrow{\text{fast}}} \text{R}'\text{Cl-AlCl}_3$$



The rate expression will be

$$\text{rate} = k_{\text{exptl}}[\text{RCl}] = k_u r[\text{RCl}] \quad (4)$$

where k_u is the unimolecular rate constant. Thus the experimental rate constant is related to the ratio of $[CH_3NO_2\text{-}AlCl_3]$ to $[CH_3NO_2]$. This means that, as long as the ratio is kept constant, addition of another inert solvent will not affect the reaction rate seriously. The change of reaction rate in this case must be due to change of polarity of the mixed solvent system whose effect is directly on the unimolecular rate constant.

For a bimolecular rearrangement by the SN2′ mechanism

$$\text{RCl-AlCl}_3 + \text{CH}_3\text{NO}_2\text{-AlCl}_3 \longrightarrow \text{CH}_3\text{NO}_2\text{-AlCl}_2^+ + \text{R}'\text{Cl} + \text{AlCl}_4^-$$
$$\text{CH}_3\text{NO}_2\text{-AlCl}_2^+ + \text{AlCl}_4^- + \text{CH}_3\text{NO}_2 \longrightarrow 2\text{CH}_3\text{NO}_2\text{-AlCl}_3$$

the rate expression will be

$$\text{rate} = k_{\text{exptl}}'[\text{RCl}][\text{CH}_3\text{NO}_2\text{-AlCl}_3]$$
$$= k_b r^2[\text{RCl}][\text{CH}_3\text{NO}_2]$$
$$= k_b r^2 s[\text{RCl}] \quad (5)$$

where k_b is the bimolecular rate constant and s is the concentration of nitromethane in the mixed solvent system. This shows that the experimental rate constant is also related to the factor of dilution with the inert solvent if the reaction mechanism is SN2′. In the isomerization of alkyl chloride, the concentration of $CH_3NO_2\text{-}AlCl_3$ is a constant, so it can be included into the experimental rate constant. Hence an experimental rate constant is to be obtained using the formula

$$\text{rate} = k_{\text{expl}}[\text{RCl}] \quad (6)$$

and both the unimolecular rate constant and the bimolecular rate constant are to be computed from the experimental rate constant by the following relations

$$k_u = k_{\text{exptl}}/r \quad (7)$$

and

$$k_b = k_{\text{exptl}}/(r^2 s) \quad (8)$$

These computed rate constants are to be checked by plots of log k *vs.* $1/T$ and of log (k/T) *vs.* $1/T$ in accord with eq 2 and 3.

In case the reaction is to be mollified by diluting the chloride by an inert solvent before the addition of aluminum chloride, the nature of the complex formed between the chloride and the dissolving aluminum chloride becomes an important factor. Aluminum chloride dissolved in an aromatic solvent such as benzene is known to be dimeric with the formula Al_2Cl_6.[9] In the complex, however, the question arises whether it is still dimeric or becomes monomeric. The corresponding equilibria are

$$\text{Al}_2\text{Cl}_6 + \text{RCl} \rightleftharpoons \text{RCl-Al}_2\text{Cl}_6$$

where

$$K = [\text{RCl-Al}_2\text{Cl}_6]/[\text{Al}_2\text{Cl}_6][\text{RCl}]$$

or

$$0.5\text{Al}_2\text{Cl}_6 + \text{RCl} \rightleftharpoons \text{RCl-AlCl}_3$$

where

$$K = [\text{RCl-AlCl}_3]/[\text{Al}_2\text{Cl}_6]^{1/2}[\text{RCl}]$$

These two possibilities give different rate expressions for the unimolecular rearrangement, *i.e.*

$$\text{rate (dimeric complex)} = -\frac{d[\text{RCl-Al}_2\text{Cl}_6]}{dt}$$
$$= k_u[\text{RCl-Al}_2\text{Cl}_6]$$
$$= k_u''[\text{RCl}][\text{Al}_2\text{Cl}_6] \quad (9)$$

and

$$\text{rate (monomeric complex)} = -\frac{d[\text{RCl-AlCl}_3]}{dt}$$
$$= k_u[\text{RCl-AlCl}_3]$$
$$= k_u'[\text{RCl}][\text{Al}_2\text{Cl}_6]^{1/2} \quad (10)$$

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(9) F. Nagy, D. Dobis, G. Litvan, and I. Telcs, *Acta Chim. Acad. Sci. Hung.*, **21**, 397 (1959).

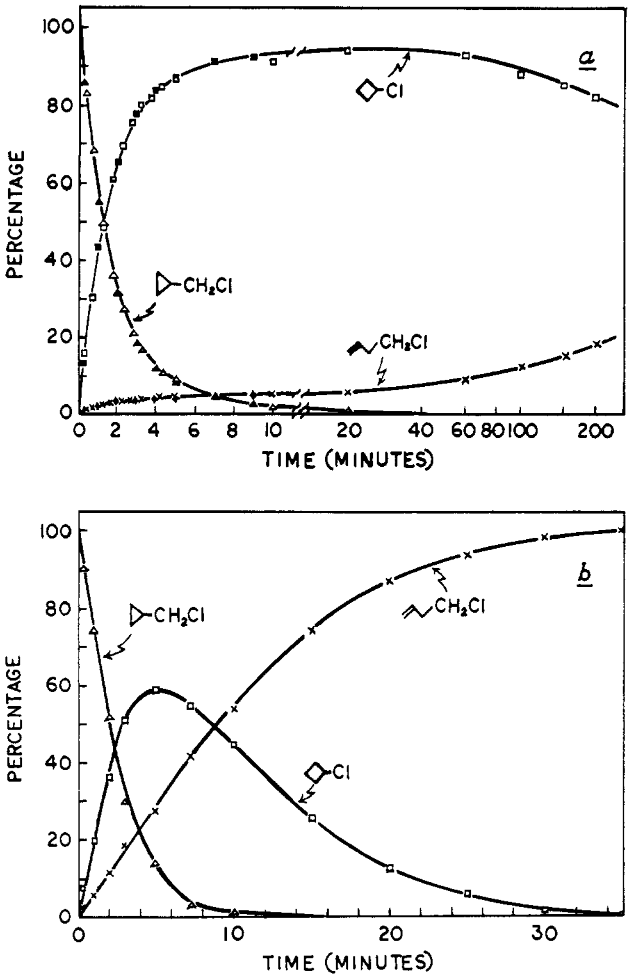


Figure 1. Typical reaction profiles for the rearrangement of cyclopropylcarbinyl chloride: a, in nitromethane–chlorobenzene mixed solvent system ($s = 9\ M$, $r = 1/100$) at $-20.0°$, two kinetic runs with different preparations of the reagent; b, in chlorobenzene at $-29.0°$ (0.04 *M* cyclopropylcarbinyl chloride, 0.007 *M* Al_2Cl_6).

where k_u'' and k_u' are products of the unimolecular rate constant, k_u, and their corresponding equilibrium constants.

For the bimolecular rearrangement, in which the nucleophilic reagent is the dimeric Al_2Cl_6 molecule, the rate expressions become

$$\text{rate (dimeric complex)} = k_b[RCl\text{-}Al_2Cl_6][Al_2Cl_6] = k_b''[RCl][Al_2Cl_6]^2 \quad (11)$$

and

$$\text{rate (monomeric complex)} = k_b[RCl\text{-}AlCl_3][Al_2Cl_6] = k_b'[RCl][Al_2Cl_6]^{3/2} \quad (12)$$

Since the concentration of dissolved aluminum chloride is constant, the reaction will be pseudo first order in RCl as before, and will give the same formula as eq 6. Thus these four rate constants will be computed from the experimental rate constant, k_{exptl}, according to eq 13–16

$$k_u'' = k_{\text{exptl}}/C \quad (13)$$

$$k_u' = k_{\text{exptl}}/C^{1/2} \quad (14)$$

$$k_b'' = k_{\text{exptl}}/C^2 \quad (15)$$

and

$$k_b' = k_{\text{exptl}}/C^{3/2} \quad (16)$$

where *C* is the concentration of Al_2Cl_6. The reaction mechanism as well as the nature of complex is expected to be found from a series of experimental data.

Rearrangement in Nitromethane–Chlorobenzene Solution. Nitromethane–chlorobenzene mixture is an ideal mixed solvent system for the kinetic study down to $-35°$. A typical kinetic plot for the rearrangement of cyclopropylcarbinyl chloride in this system at $-20.0°$ is shown in Figure 1a. No polymerization or elimination reactions were observed below $-20°$. Rearrangement of cyclobutyl chloride is much slower, and no rearrangement of allylcarbinyl chloride was observed. The kinetic runs were highly reproducible except those below $-34°$ or above $-17°$. The rate of conversion of the starting chloride is strictly first order in the chloride concentration.

Cyclopropylcarbinyl chloride rearranges to both cyclobutyl and allylcarbinyl chlorides. The experimental rate constants for their formations are obtained from the kinetic plots. The corresponding unimolecular rate constants, k_u, and bimolecular rate constants, k_b, are computed with the relations $k_u = k_{\text{exptl}}/r$ and $k_b = k_{\text{exptl}}/(r^2s)$. Results are shown in Table I. The plots of computed bimolecular rate constants *vs.* temperature with different *r* values and the same *s* value meet to give a single line. Since the same *s* value means the same polarity of the medium, this result indicates that the mechanism of these rearrangements is bimolecular.

In the temperature range of -33 to $-17°$ the Arrhenius plots of the bimolecular rate constants gave straight lines for these rearrangements. The obtained Arrhenius activation energies are 18.7 and 20.4 kcal/mol, respectively, for rearrangements to cyclobutyl chloride and to allylcarbinyl chloride. The rate constants are both about twice as large in the system with 3 *M* nitromethane as they are in the system with 9 *M* nitromethane. This acceleration in the less polar solvent system supports a noncarbonium ion transition state, *i.e.*, an SN2′ mechanism. The Arrhenius expressions of these rate constants are

$$k_{1b} = \begin{matrix} 10^{20.84}e^{-18,700/RT}\ M^{-1}\ sec^{-1} & (s = 9\ M) \\ 10^{21.17}e^{-18,700/RT}\ M^{-1}\ sec^{-1} & (s = 3\ M) \end{matrix}$$

and

$$k_{2b} = \begin{matrix} 10^{20.94}e^{-20,400/RT}\ M^{-1}\ sec^{-1} & (s = 9\ M) \\ 10^{21.28}e^{-20,400/RT}\ M^{-1}\ sec^{-1} & (s = 3\ M) \end{matrix}$$

Assuming that the transition state exists in equilibrium with the initial system consisting of RCl, CH_3NO_2, and $CH_3NO_2\text{-}AlCl_3$, the entropy of activation, $\Delta S^{\ddagger}$, and the enthalpy of activation, $\Delta H^{\ddagger}$, can be obtained from the plot of log (k_b/T) *vs.* $1/T$ in accord with the rate constant expression $(kT/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$ of the absolute rate theory. For the rearrangement of cyclobutyl chloride (Figure 2), they are

$$\Delta H_1^{\ddagger} = \begin{cases} 17.9 \text{ kcal/mol} & (s = 9\ M) \\ 17.6 \text{ kcal/mol} & (s = 3\ M) \end{cases}$$

and

$$\Delta S_1^{\ddagger} = \begin{cases} 3.35 \text{ eu} & (s = 9\ M) \\ 34.0 \text{ eu} & (s = 3\ M) \end{cases}$$

Table I. Experimental and Computed Rate Constants for the Rearrangement of Cyclopropylcarbinyl Chloride to Cyclobutyl Chloride (k_1) and to Allylcarbinyl Chloride (k_2) in Nitromethane–Chlorobenzene Mixed Solvent System

No.	Temp, °C	s, M	r	$k_{1\text{exptl}}$, min^{-1}	$k_{1\text{u}}$, min^{-1}	$k_{1\text{b}}$, M^{-1} min^{-1}	$k_{2\text{exptl}}$, min^{-1}	$k_{2\text{u}}$, min^{-1}	$k_{2\text{b}}$, M^{-1} min^{-1}
1	−33.0	9.0	1/50	0.314	15.7	87.2	0.0121	0.605	3.36
2	−29.0	9.0	1/50	0.628	31.4	175	0.0262	1.31	7.26
3	−24.0	9.0	1/50	1.30	65.0	361	0.0590	2.95	16.4
4	−24.0	9.0	1/100	0.322	32.2	358	0.0153	1.53	17.0
5	−20.0	9.0	1/100	0.558	55.8	621	0.0263	2.63	29.2
6	−17.0	9.0	1/100	0.955	95.5	1070	0.0460	4.00	51.0
7	−15.0	9.0	1/100	2.30	230	2560	0.121	12.1	134
8	−33.0	3.0	1/50	0.206	10.3	172	0.0092	0.46	7.61
9	−28.5	3.0	1/50	0.482	24.1	402	0.0227	1.13	18.9
10	−25.8	3.0	1/50	0.701	35.0	584	0.0330	1.65	27.5
11	−20.0	3.0	1/50	1.54	77.0	1283	0.0765	3.78	63.0
12	−20.0	3.0	1/100	0.287	28.7	956	0.0166	1.66	55.3

For the rearrangement to allylcarbinyl chloride (Figure 3), they are

$$\Delta H_2^{\ddagger} = \begin{cases} 19.8 \text{ kcal/mol} & (s = 9\ M) \\ 19.5 \text{ kcal/mol} & (s = 3\ M) \end{cases}$$

and

$$\Delta S_2^{\ddagger} = \begin{cases} 35.0 \text{ eu} & (s = 9\ M) \\ 35.4 \text{ eu} & (s = 3\ M) \end{cases}$$

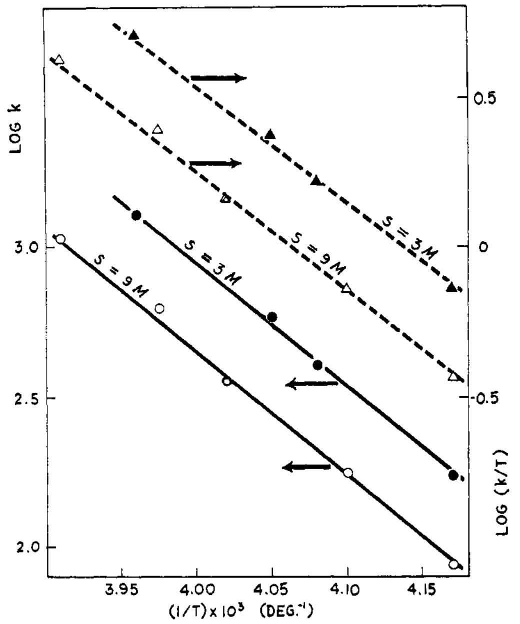


Figure 2. Arrhenius plots (solid lines) and plots of log (k/T) *vs.* $1/T$ (broken lines) for the rearrangement of cyclopropylcarbinyl chloride to cyclobutyl chloride in nitromethane–chlorobenzene mixed solvent system.

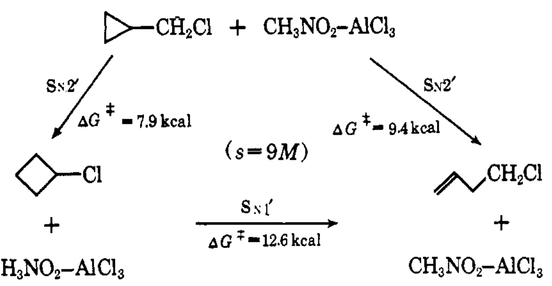
Cyclobutyl chloride rearranges to allylcarbinyl chloride. The results of kinetic studies (Table II) indicate that the rearrangement in the solvent system with $s = 9\ M$ is unimolecular but in a less polar medium ($s = 3\ M$) contribution from a bimolecular mechanism exists. The computed unimolecular rate constants increase as the polarity of the solvent system increases. This is a rather clear indication that the unimolecular rearrangement is an S$_\text{N}$1′ mechanism with a carbonium ion intermediate and is not an S$_\text{N}$i′ mechanism. Arrhenius plot gave the following rate constant expression which shows 27.3 kcal/mol of activation energy.

$$k_{3\text{u}} = 10^{24.6}e^{-27{,}300/RT}\ \text{sec}^{-1}\ (s = 9\ M)$$

The plot is shown in Figure 4.

The enthalpy of activation and the entropy of activation are also obtained from the plot of log (k_u/T) *vs.* $1/T$. These are $\Delta H_3^{\ddagger} = 27.1$ kcal/mol and $\Delta S_3^{\ddagger} = 48.7$ eu ($s = 9\ M$). The large difference in this entropy value from those in the rearrangement of cyclopropylcarbinyl chloride is another indication for the difference in their mechanisms.

The free energies of activation of all these rearrangement reactions computed for 25° are illustrated in the following diagram.



Rearrangement in Nitromethane Solution. To see whether cyclobutyl chloride rearranges to cyclopropylcarbinyl chloride, a kinetic study was conducted at +20 to +40° in nitromethane solution. Considerable decomposition takes place at the instant of mixing which uses up a large portion of the starting chloride. Besides

Table II. Experimental and Computed Rate Constants for the Rearrangement of Cyclobutyl Chloride to Allylcarbinyl Chloride (k_3) in Nitromethane–Chlorobenzene Mixed Solvent System

No.	Temp, °C	s, M	r	$k_{3\text{exptl}}$, min^{-1}	$k_{3\text{u}}$, min^{-1}	$k_{3\text{b}}$, M^{-1} min^{-1}
13	−24.8	17	1/10	0.00634	0.0634	0.0373
14	−24.8	9	1/10	0.00578	0.0578	0.0643
15	−24.0	9	1/50	0.00122	0.0610	0.339
16	−20.0	9	1/50	0.00295	0.1475	0.820
17	−15.0	9	1/10	0.0420	0.420	0.467
18	−25.8	3	1/50	0.000244	0.0122	0.203
19	−20.0	3	1/50	0.000760	0.0380	0.633
20	−15.0	3	1/50	0.00238	0.119	1.98
21	−15.0	3	1/10	0.0238	0.238	0.792

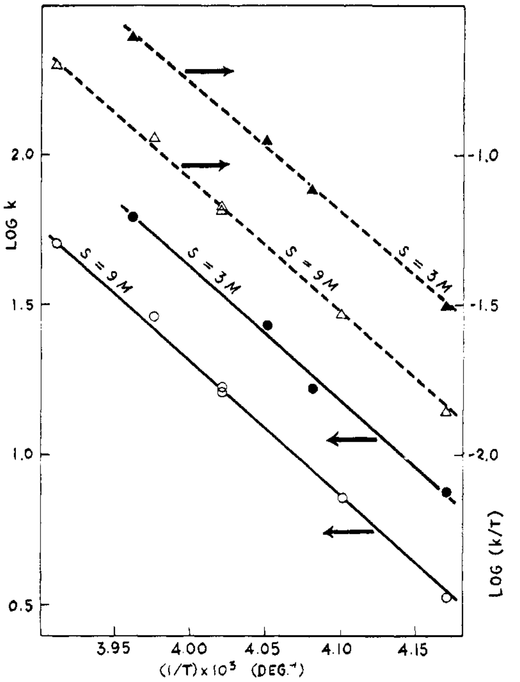


Figure 3. Arrhenius plots (solid lines) and plots of log (*k*/*T*) *vs.* 1/*T* (broken lines) for the rearrangement of cyclopropylcarbinyl chloride to allylcarbinyl chloride in nitromethane–chlorobenzene mixed solvent system.

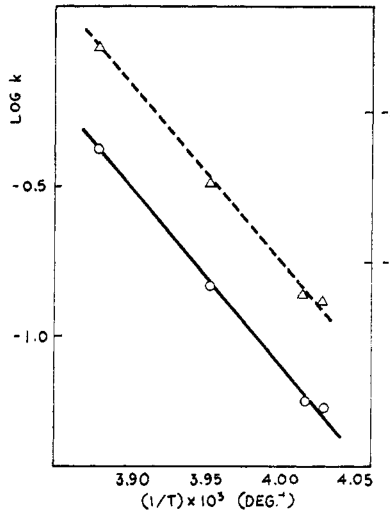
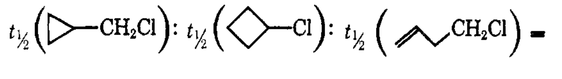


Figure 4. Arrhenius plot (solid line) and the plot of log (*k*/*T*) *vs.* 1/*T* (broken line) for the rearrangement of cyclobutyl chloride to allylcarbinyl chloride in nitromethane–chlorobenzene mixed solvent system (*s* = 9 *M*).

the expected rearrangement, substantial polymerization takes place simultaneously resulting in the formation of brown polymers.

When allylcarbinyl chloride is the starting compound, polymerization is the only reaction observed. The plot of [allylcarbinyl chloride]$_0$/[allylcarbinyl chloride]$_t$ *vs.* time gave a straight line which indicates second-order kinetics. In the case of cyclopropylcarbinyl chloride, the order of the polymerization was also obtained as the same from the slope of a plot of log (−d[total chlorides]/d*t*) *vs.* log [total chlorides] which is a straight line of a slope exactly 2.0 until *ca.* 70% of the cyclopropylcarbinyl chloride is consumed. The same plot in cyclobutyl chloride was no longer a straight line; the initial slope was smaller than 2.7 which seems to suggest that it is similarly second order in this chloride, but the polymerization rate is very much smaller than those of other chlorides formed through rearrangement. Relative half-lives observed for polymerizations of these three chlorides at 40° are



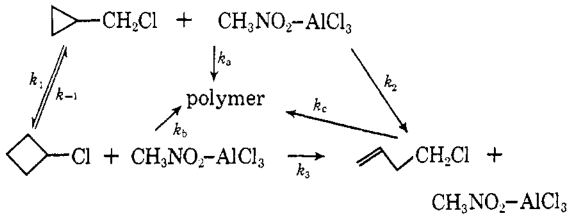
1 : 1.7 x 10^5 : 2.3 x 10^2

Kinetic studies on the rearrangement reactions of the chlorides showed that the simultaneous polymerization does not affect the kinetic curves appreciably. This means that the polymer formed does not inhibit the course of the isomerization reaction, which is frequently the case in other rearrangement reactions.[10]

The rearrangement of cyclobutyl chloride to cyclopropylcarbinyl chloride is clearly observed between 20 and 40°. The relative rate of this rearrangement compared to that of the rearrangement to allylcarbinyl chloride from cyclobutyl chloride increases as the temperature is raised. This indicates a high activation energy for this rearrangement. Estimation of this energy value by the comparison of the rate ratio of the formation of cyclopropylcarbinyl chloride and that of allylcarbinyl chloride at 30 and 40° gave 45 kcal/mol.

The rearrangement of cyclopropylcarbinyl chloride to cyclobutyl and allylcarbinyl chloride was also studied at this temperature range. Results are in Table III.

The over-all reaction scheme with the relative rate constants at 40° is



$k_1 : k_{-1} : k_2 : k_3 = 1 : 0.36 : 1.2 \times 10^{-4} : 5.2 \times 10^{-3}$

$k_a : k_b : k_c = 1 : 6 \times 10^{-6} : 4.5 \times 10^{-3}$

Rearrangement in Chlorobenzene Solution. Although aluminum chloride is scarcely soluble, the aluminum chloride complex of the alkyl chloride dissolves well in chlorobenzene. Thus the reaction of pulverized aluminum chloride with cyclobutyl chloride in chlorobenzene shows an initial slow period before the reaction mixture becomes clear and homogeneous. After the equilibrium between dissolved aluminum chloride and the cyclobutyl chloride–aluminum chloride complex is attained, the reaction keeps a steady first-order rate in cyclobutyl chloride concentration. Eight individual kinetic runs in the temperature range of −41 to −20° are shown in Table IV. The results illustrate considerable fluctuation due to the limitation of the system. Among those four computed rate constants, the unimolecular rate constant for dimeric complex, k_u'', seems to be the most reasonable one if expt 30 is deemed

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(10) B. L. Everling, "Advances in Catalysis and Related Subjects," Vol. VI, Academic Press, New York, N. Y., 1954, pp 209–211; G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 729 (1963).

Table III. Experimental Rate Constants for the Rearrangement in Nitromethane by Water-Deactivated Aluminum Chloride (Initial Concentration, 0.1 *M*)[a]

No.	Temp, °C	Starting compd	$k_{1\mathrm{exptl}}$, min^{-1}	$k_{-1\mathrm{exptl}}$, min^{-1}	$k_{2\mathrm{exptl}}$, min^{-1}	$k_{3\mathrm{exptl}}$, min^{-1}	k_1/k_2	k_{-1}/k_3
22	21.0	c-$C_3H_5CH_2Cl$	2.5×10^{-4}		Nil			
23	30.0	c-$C_3H_5CH_2Cl$	1.03×10^{-2}		Nil			
24	30.0	c-C_4H_7Cl		3.5×10^{-4}		3.5×10^{-5}		10
25	35.0	c-$C_3H_5CH_2Cl$	2.1×10^{-2}		3×10^{-3}		7.0	
26	40.0	c-$C_3H_5CH_2Cl$	7×10^{-2}		1×10^{-2}		7.0	
27	40.0	c-C_4H_7Cl		5.5×10^{-2}		7.8×10^{-4}		71

[a] See Experimental Section.

Table IV. Experimental and Computed Rate Constants for the Rearrangement of Cyclobutyl Chloride in Chlorobenzene

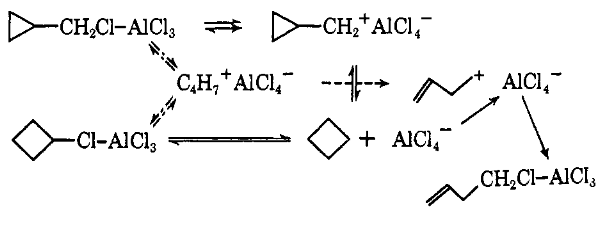
No.	Temp, °C	Al_2Cl_6, 10^{-4} *M*	$k_{3\mathrm{exptl}}$, min^{-1}	k_u'', M^{-1} min^{-1}	k_u', $M^{-1/2}$ min^{-1}	k_b'', M^{-2} min^{-1}	k_b', $M^{-3/2}$ min^{-1}
28	−41.0	19.1	0.0108	5.65	0.247	2.96×10^3	1.29×10^2
29	−40.0	19.1	0.0148	7.75	0.339	4.05×10^3	1.77×10^2
30	−40.0	33.1	0.318	96.2	5.56	2.91×10^4	1.68×10^3
31	−25.0	8.1	0.0795	98.2	2.79	1.21×10^5	3.44×10^3
32	−25.0	47.2	0.5	106	7.47	2.25×10^4	1.56×10^3
33	−25.0	52.7	0.7	133	9.65	2.51×10^4	1.83×10^3
34	−20.0	48.0	1.54	321	22.5	6.68×10^4	4.68×10^3
35	−20.0	42.7	1.75	410	26.8	9.62×10^4	6.28×10^3

as an exceptional failure. The Arrhenius plot based on this rate constant as well as the plot of log (k_u''/T) *vs.* $1/T$ is shown in Figure 5. The Arrhenius expression for this rate constant is $k_u'' = 10^{23.2}e^{-22,000/RT}$ M^{-1} sec^{-1} and the enthalpy and the entropy of activation are $\Delta H^{\ddagger} = 21.4$ kcal/mol and $\Delta S^{\ddagger} = 46.0$ eu as obtained from these plots. The entropy of activation is only 5% smaller than that obtained in the mixed solvent system (48.7 eu), but the enthalpy of activation is remarkably smaller than the latter case (27.1 kcal/mol). This result seems to be caused by the difference in the states of the aluminum chloride reagent in both cases.

The same study of the isomerization of cyclopropylcarbinyl chloride resulted in very poor reproducibility owing to the much higher reactivity of this chloride. An example of this kinetic run is shown in Figure 1b. From many repeated kinetic runs, it was found that the rate of rearrangement of cyclopropylcarbinyl chloride to cyclobutyl chloride is roughly proportional to the square of aluminum chloride concentration. This suggests that the mechanism of this rearrangement is bimolecular on the dimeric complex.

Discussion and Conclusions

In Friedel–Crafts processes, the reaction may proceed through an ionic intermediate or through a polarized complex. The aluminum chloride catalyzed rearrangement of cyclopropylcarbinyl chloride and cyclobutyl chloride may, therefore, be caused by the rearrangement of their corresponding carbonium ions through a low-energy barrier as suggested by the ready rearrangement equilibrium in many S$_N$1 reactions of their derivatives or through an energetically favored common nonclassical carbonium ion. Thus the mechanism should be



where $C_4H_7^+$ represents the common nonclassical carbonium ion. In this mechanism, the observed kinetics should be always first order regardless of which step is rate determining. If the ionization steps are the rate-determining ones, the transition states for rearrangements starting from different chlorides must differ. If the rearrangements step is the rate-determining one, then the transition state should be the same. Thermodynamically controlled product may be expected in the former case, and kinetically controlled product in the latter. Comparison of the enthalpy of activation can be also used for this differentiation.

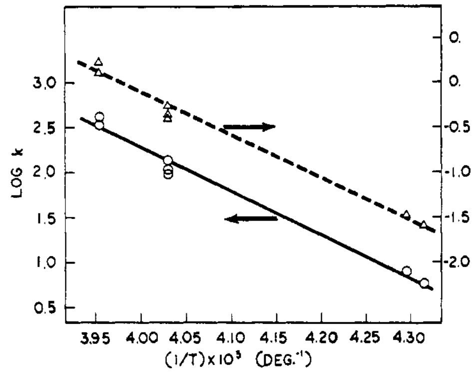
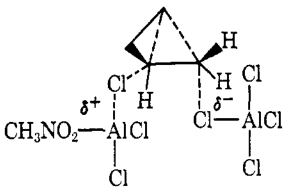


Figure 5. Arrhenius plot (solid line) and plot of log (k/T) *vs.* $1/T$ (broken line) for the rearrangement of cyclobutyl chloride to allylcarbinyl chloride in chlorobenzene.

It is generally believed that cyclopropylcarbinyl derivatives are very easily ionized through neighboring group participation of the cyclopropyl group or through formation of a nonclassical carbonium ion.[2] This is also believed to be the sole reason for the especially high reactivity of compounds with an α-cyclopropyl group. In the comparison of rearrangement reactions of cyclopropylcarbinyl chloride and of cyclobutyl chloride, therefore, it could be expected that the former should have a higher tendency for a carbonium ion mechanism than the latter. Our present study, however, showed the contrary: the more readily ionizable cyclopropylcarbinyl chloride showed an SN2′ mechanism with a noncarbonium ion type of intermediate while cyclobutyl chloride showed a larger tendency for SN1′ mechanism in the rearrangement reaction.

The rearrangement of cyclopropylcarbinyl chloride is thus caused by the attack of a molecule of the reagent on the aluminum chloride complex. The transition state in the rearrangement to cyclobutyl chloride may look like



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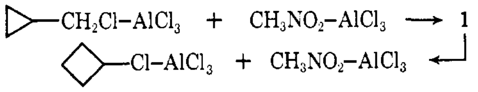
In this structure, a cleaving C–C σ bond is compensated by a forming C–C σ bond and also by the release of partial ring strain. The rearrangement follows the mechanism

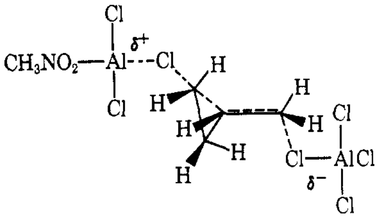


The tendency for this bimolecular mechanism seems to suggest that when cyclopropylcarbinyl chloride is complexed with aluminum chloride the increased inductive effect of the chlorine atom bestows on the adjacent carbon atom a considerable positive charge which eventually diffuses into the cyclopropyl ring. A recent study on the epr spectra of alkyl- and cyclopropylketyls showed a strong electrophilic character on the cyclopropyl group.[11] Similarly, potassium-treated cyclopropylbenzene has a considerable degree of delocalization of the odd electron on the cyclopropyl group indicative of the π character of the cyclopropane ring which allows conjugation with an adjacent π-orbital system or a p orbital. No such phenomenon was reported for cyclobutyl compounds. In other words, the above result seems to be good evidence for the conjugation phenomenon displayed by the cyclopropyl ring with the adjacent carbon atom which bears a partial cationic character.

Assuming that the enthalpy difference of the aluminum chloride complexes of cyclopropylcarbinyl chloride and cyclobutyl chloride is mainly due to the difference in their ring strain energies, it can be considered that the aluminum chloride complex of cyclobutyl chloride is only about 1.5 kcal/mol more stable than that of cyclopropylcarbinyl chloride.[12] This implies that the SN2′ rearrangement of cyclobutyl chloride to cyclopropylcarbinyl chloride should have an enthalpy of activation of about 19 kcal/mol estimated from the observed values, 17.9 and 17.6 kcal/mol, for the reverse rearrangement. This is considerably smaller than that of the SN1′ rearrangement of cyclobutyl chloride to allylcarbinyl chloride, *i.e.*, 27.1 kcal/mol, which was observed. The difficulty for the observation of the former rearrangement must be due to a small entropy of activation which makes its free energy of activation much larger than that of the latter rearrangement, *i.e.*, 12.6 kcal/mol at 25°.

Roberts, *et al.*,[5] reported the observation of a probable equilibrium between cyclopropylcarbinyl and cyclobutyl chlorides under the presence of zinc chloride at 25° whose approximate composition is 1:36 in favor of cyclobutyl chloride. This alludes to the reversibility of the rearrangement as well as a free energy difference between these two chlorides of about 2 kcal/mol, in agreement with the above estimation. But if the catalytic behavior of zinc chloride is considered similar to that of aluminum chloride, the reversibility of the suggested equilibrium will become questionable from the above consideration of the entropy factor. To clarify this point, we have studied the same rearrangement with zinc chloride as the catalyst. Our results showed a constant decrease of the cyclobutyl chloride concentration after it reached a maximum, as well as a constant increase of allylcarbinyl chloride. The implication is that we are dealing with consecutive reactions in which cyclopropylcarbinyl chloride rearranges rather fast to cyclobutyl chloride which in turn rearranges slowly to allylcarbinyl chloride. The mechanistic features are similar to those of the aluminum chloride catalyzed rearrangement. In another paper Roberts himself reported that the equimolar mixture of anhydrous zinc bromide and 48% hydrobromic acid isomerizes a 2:1 mixture of cyclopropylcarbinyl and cyclobutyl bromides giving after 1 hr at 0° a mixture of 30% cyclobutyl bromide and 70% allylcarbinyl bromide, but 100% allylcarbinyl bromide at room temperature.[3] This observation is consistent with the rearrangement scheme observed in our present work for the chlorides.

The observed SN2′ rearrangement of cyclopropylcarbinyl chloride to allylcarbinyl chloride may have a transition state like



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This structure is analogous to that suggested by Julia, *et al.*, in the stereospecific rearrangement of secondary cyclopropylcarbinols to the corresponding *trans*-bromo olefins by hydrobromic acid.[13] High stereospecificity which suggests a similar transition state was also observed recently by Johnson, *et al.*, in the rearrangement of a mixture of some secondary cyclopropylcarbinyl and cyclobutyl bromides by zinc bromide.[14] They suggested that the high stereospecificity is consistent with a concerted process involving attack by bromide ion.

The entropy increase in the above rearrangement is not appreciably different from the rearrangement to cyclobutyl chloride, but the enthalpy of activation is about 2 kcal/mol larger. This seems to be caused by

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(11) R. G. Kostyanovskii, S. P. Solodovnikov, and O. A. Yuzhakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 735 (1966).

(12) Sj. Koarsemaker and J. Coops, *Rec. Trav. Chim. Pays Bas*, 71, 261 (1952).

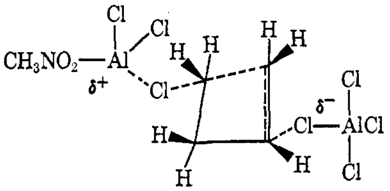
(13) M. Julia, S. Julia, and S.-Y Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961).

(14) S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, 90, 2882 (1968).

the fact that in this case the cleaving C–C σ bond is compensated by a forming C–C π bond instead of a σ bond.

The large difference in activation energies of the rearrangement of cyclobutyl chloride in nitromethane, presumably by an SN1′ mechanism, to cyclopropylcarbinyl chloride and allylcarbinyl chloride, namely, *ca.* 45 and 27.3 kcal/mol, seems to indicate that the rate-determining step is not always the ionization step. At least for the rearrangement leading to cyclopropylcarbinyl chloride, the rate-determining step should lie after the ionization step, because in this case the activation energy is much larger than for the rearrangement leading to allylcarbinyl chloride. In the latter case the rate-determining step can be either the ionization step or the subsequent rearrangement. As discussed previously, the initial system on which the observed activation energy is to be based is the system composed of uncomplexed cyclobutyl chloride and the aluminum chloride–nitromethane complex. Two energy diagrams with classical or nonclassical carbonium ion intermediates are shown in Figure 6 to illustrate this view. In these diagrams, T_{-1} is the energy peak for the rearrangement to cyclopropylcarbinyl chloride while either T_3 or T_3' is that for the rearrangement to allylcarbinyl chloride; the energy difference between the initial state and the energy peak is the corresponding energy of activation.

The transition state of an SN2′ rearrangement of cyclobutyl chloride to allylcarbinyl chloride which takes place in less polar medium may be



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Activation parameters for this rearrangement were not obtained. Assuming that the entropy of activation is similar to that in the SN2′ rearrangement of cyclopropylcarbinyl chloride to cyclobutyl chloride and also that the free energy of activation is comparable to its own SN1′ rearrangement so that these two mechanisms could compete, the enthalpy of activation can be estimated as about 23.5 kcal/mol which is lower than the enthalpy of activation in the SN1′ rearrangement (27.1 kcal/mol). This suggests that cyclobutyl chloride will show more carbonium ion type reaction at higher temperature than at lower temperature.

Concerning the nature of the aluminum chloride complexes of alkyl halides in chlorobenzene and the mechanisms of their rearrangements, the evidence obtained in the present work is not clear-cut, but again results suggest the following possible pathways without the necessity of a common "nonclassical" carbonium ion intermediate.

In the carbonium ion type rearrangement of cyclobutyl chloride to allylcarbinyl chloride, the entropy of activation (46.0 eu) was not too much different from that when the reagent is the aluminum chloride–nitromethane complex (48.7 eu). This suggests that the entropy change by the increased internal rotation of the Al–Cl bond in the former is comparable to the translational entropy increase in the latter in which the initial state is cyclobutyl chloride and CH_3NO_3–$AlCl_3$ and the intermediate state is cyclobutyl cation, $AlCl_4^-$, and CH_3NO_2. The enthalpy of activation is much larger in the latter case. This is due to the cleavage of the O–Al bond of the complex.

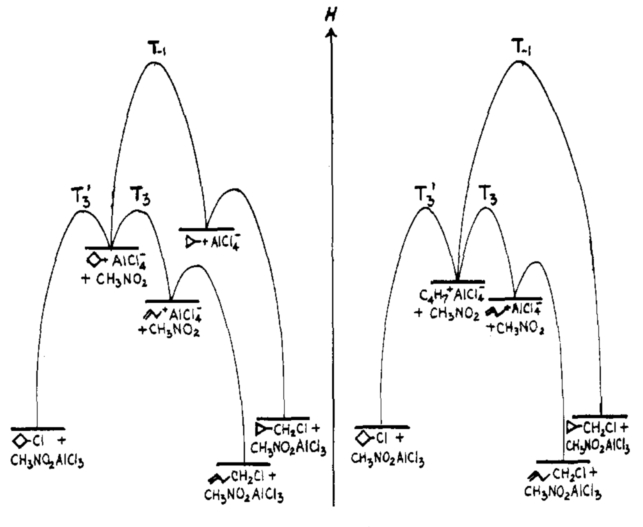
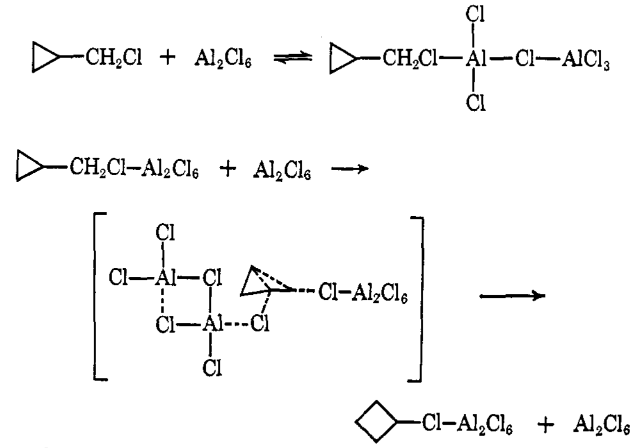


Figure 6. Energy profiles for the isomerization of cyclobutyl chloride with classical carbonium ion intermediates (left) and with nonclassical carbonium ion intermediates (right).



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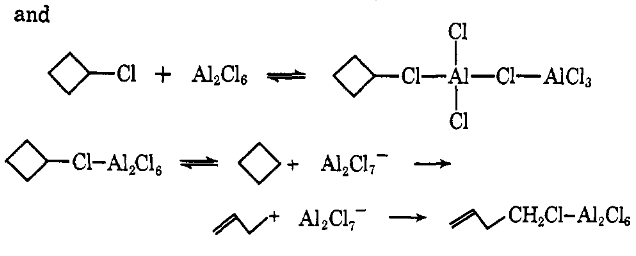

Experimental Section

Preparation of Cyclopropylcarbinyl, Cyclobutyl, and Allylcarbinyl Chlorides. Commercial cyclopropylcarbinol was treated with pyridine and thionyl chloride below ice temperature. The reaction temperature is not very crucial for the later separation of the mixed product. The reaction product was washed with ice water, neutralized with solid potassium carbonate, and dried with anhydrous sodium sulfate. Repeated preparative gas chromatography with an Aerograph Autoprep 700 gave both cyclopropylcarbinyl chloride and cyclobutyl chloride in higher than 99.5% purity by analytical gas chromatography. The same treatment of 3-buten-1-ol gave allylcarbinyl chloride with little contamination from other chlorides. Preparative gas chromatography gave practically 100% pure allylcarbinyl chloride. The boiling points were as follows: cyclopropylcarbinyl chloride, 87.5° (lit.[4] bp 87–89°); cyclobutyl chloride, 80.2° (lit.[4] bp 82–83°); and allylcarbinyl chloride, 71.1° (lit.[4] bp 73–74°). Identification was made with their nmr and ir spectra.

Solvents. Solvents of ACS Reagent Grade or Spectroquality Grade were used. They were purified by standard procedures whenever necessary. For the present purpose, the purified solvent was washed several times with distilled water and dried first over anhydrous sodium sulfate and then over activated Type 5A Molecular Sieves for 1 day at −5°. This was distilled with equipment baked at 160° for longer than 24 hr before use. The distillate was stored in a baked bottle with Type 4A Molecular Sieves at −5°.

Aluminum Chloride Solution. A stock solution of r equals 1/10 was prepared by dissolving pulverized aluminum chloride (Matheson Coleman and Bell, ACS Reagent Grade) from a newly opened bottle in nitromethane strictly purified as stated above. A colorless solution was obtained. A gentle stream of dry nitrogen gas was applied to expel the hydrogen chloride gas possibly accumulated in the aluminum chloride bottle before use. It was also applied to substitute nitrogen for the air in the bottle of aluminum chloride stock solution. This solution was stored at −5°. The activity of this solution stayed nearly constant for more than 1 week, proven by the amazingly high reproducibility of kinetic runs, one example of which can be seen in Figure 1a. For reactions above room temperature for which diminished aluminum chloride activity is desired, the aluminum chloride solution was prepared by dissolving a portion of aluminum chloride in nitromethane which was dried over anhydrous sodium sulfate. The water content which is in equilibrium with hydrous sodium sulfate crystals in the bottle effectively diminishes the aluminum chloride activity. After 2 days at room temperature, the activity reached adequate stability for the kinetic study. An initial concentration of 0.1 M was found most adequate.

Kinetic Runs. The aluminum chloride solution and the additional inert solvent were placed in a thermostated reaction bottle with a magnetic stirrer and a thermometer and connected to a dry nitrogen stream. The temperature stability was kept to within 0.1° inside the reaction mixture even at −40°. A solution of the reactant in nitromethane or in the inert solvent was kept at the same temperature and was introduced to the reaction bottle after both reached the desired temperature. A small portion of the reaction mixture was drawn out from time to time with a glass dropper cooled with Dry Ice–acetone under nitrogen gas flow. The reaction mixture was quenched with ice-cold distilled water saturated with n-butyl alcohol which secured the maximum efficiency for both instant quenching and the later analysis of the reaction mixture. Solid anhydrous sodium sulfate was then introduced to break the emulsion and to salt out the portion of organic chloride in the water layer. Analysis of the mixture was made by a Perkin-Elmer Model 226 gas chromatograph with an Infotronic Model CRS-1 chromatograph readout system and a Victor Digit-matic printer. The quenched reaction mixture was kept in an ice bath while waiting for analysis.

The reaction is especially sensitive to moisture and other oxygen-containing organic substances, such as alcohols, ethers, and ketones. No activation effect was observed on the introduction of very small amounts of water as in ordinary Friedel–Crafts and related reactions. The effect is seriously deactivating. Contamination of a metallic ion from a broken magnetic stirrer was found to accelerate the reaction above room temperature, but no systematic study on this problem was carried out. Careful elimination of all possible influencing factors made it possible to bring the reproducibility of the kinetic runs within the range of better than 3% error in the consumption rate constants.

For gas chromatographic analyses, a 150-ft Golay column with either diethylene glycol succinate or Carbowax K1540 was used. The column temperature was kept at 60–70° and the injection temperature 100–150°. These conditions give a reproducibility of analysis of better than ±1% for the main component and ±10% for the minor component of the chloride mixture. That no appreciable change in composition of the solutions took place in the injection block or the column was checked carefully with simulated solutions of known composition.

The kinetic runs in chlorobenzene were carried out as follows. Weighed portions of aluminum chloride were added to the thermostated chlorobenzene with vigorous stirring under dry nitrogen gas. After 10 min, a solution of the reactant in chlorobenzene at the same temperature was introduced and the kinetic run started. The kinetic plot generally shows an unstabilized preequilibrium period of 2–5 min depending on the quantity of aluminum chloride, the temperature, the efficiency of stirring, and other factors. Kinetic data were taken from the later portion of the plot.

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Syntheses and Coordination Ability of Some 1,5-Cyclopolymethylenetetrazoles[1]

Frank M. D'Itri[2] and Alexander I. Popov

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received April 12, 1968*

Abstract: A series of 1,5-cyclopolymethylenetetrazoles were synthesized with the hydrocarbon chain containing 3, 4, 6, 7, 8, 9, and 11 methylene groups. The donor properties of these compounds were investigated by spectrophotometric measurements of the tetrazole–iodine charge-transfer complex formation constants in the 5–35° interval. The solvent was 1,2-dichloroethane. The enthalpy and the entropy changes for the complexing reactions were determined from the temperature coefficient of the stability constant. The donor properties of tetrazoles were rather weak and the formation constant values at 25° ranged from 1.42 to 2.64 l. mol^{-1}. There does not seem to be a simple correlation between the length of the hydrocarbon chain and the stability of the iodine complex.

Although the chemical properties of pentamethylenetetrazole (I) have been rather thoroughly studied by a number of investigators, surprisingly the lower homologs of pentamethylenetetrazole have not been investigated to any significant extent. In fact, literature search indicates that there exists only one report on the preparation of tri- and tetramethylenetetrazole (C_3MT and C_4MT, respectively)[3] and another similar

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(1) Abstracted from the Ph.D. Dissertation of Frank M. D'Itri, Michigan State University, 1968.

(2) Socony-Mobil Fellow, 1967–1968.

(3) von Kereszty and Wolf, German Patent 611,692; *Chem. Abstr.*, **29**, 5994 (1935); U.S. Patent 2,008,536; *Chem. Abstr.*, **29**, 5604 (1935).