The kinetics of thermal isomerization of 3,3-dihalo-1,2-diphenylaziridines containing fluorine, chlorine, or bromine atoms in the ring were studied, and the activation parameters of the reaction were determined. A concerted mechanism for the formation of imidoyl halides from haloaziridines that includes conrotatory opening of the aziridine ring with halogen migration of the 1,2 type is proposed on the basis of the data obtained.

In [1-6] it is shown that when C-chloro-substituted aziridines are heated, a chlorine atom migrates to the adjacent carbon atom with simultaneous opening of the opposite C-N bond and the formation of imidoyl halides. Halogen-containing N-aminoaziridines are converted to aldehyde hydrazones via the same scheme [7].

A transition state with ionic character has been proposed on the basis of a study of the kinetics of thermal isomerization of 3,3-dichloro- and 3,3-dibromo-1,2-diphenylaziridines (I, II) [5]. In the present research we investigated the isomerization of aziridines III-VI containing different halogen atoms in the ring. The phenyl groups in the investigated aziridines are trans-oriented [8, 9].

The corresponding imidoyl halides IX-XI are obtained when solutions of aziridines III-VI in CCl₄ or C₂Cl₄ are heated. Only IX was obtained from aziridines III and IV, while X and XI, respectively, were obtained from aziridines V and VI. The structure of the imidoyl halides was confirmed by spectral methods (Table 1) and by hydrolysis to phenylhaloacetic acid anilides XII and XIII. 2-Chloro-2-phenylacetanilide (XII) is formed in quantitative yield by hydrolysis of imidoyl halide X and VII, and 2-bromo-2-phenylacetanilide (XIII) is formed by hydrolysis of VIII, IX, and XI.

As in the case of aziridines I and II [5], the rates of thermal isomerization of aziridines III-VI were determined by IR and PMR spectroscopy: in the first case from the change in the intensity of the band at ~1400 cm⁻¹, and in the second case from the change in the intensity of the signals of the aziridine proton at 3.5-3.7 ppm and the methylidyne proton of imidoyl halides VIII-XI at 5.5-5.9 ppm. It was found that the kinetics of isomerization of the aziridines correspond to a first-order reaction. According to the PMR data, the rates of consumption of the aziridine and accumulation of the imidoyl halide are identical (Table 2). Special experiments demonstrated that the isomerization rate constant increases when the aziridine concentration in solution is increased above 2%. The rate constants for the isomerization of aziridines III and IV were determined by a study of mixtures of the same compounds containing 88 and 60% aziridine III (Table 2).

It is apparent from the data in Table 3 that the rate of thermal isomerization of the aziridines depends on both the nature of the halogens and on their position relative to the other substituents in the aziridine ring. With respect to their ability to undergo migration the halogens can be arranged in the order Br > Cl > F, which corresponds to the order of strengths of carbon–halogen bonds [10]. It follows from a comparison of the rates of isomerization of aziridines III and IV that a bromine atom that is syn-oriented with respect to the unshared electron pair of the nitrogen atom migrates more readily.* In addition, the migration of a halogen from a

*The orientation of the halogen is subsequently defined in the text relative to the unshared electron pair of the nitrogen atom.
TABLE 1. Spectral Characteristics of N-Phenyl-2-halo-2-phenylacetimidoyl Halides (IX–XI)*

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV spectrum</th>
<th>Absorption bands in the IR spectrum, cm⁻¹</th>
<th>PMR spectrum, δ, ppm (J, Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nmax, nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>1685 s</td>
<td>225 (4,20), 272 (4,25)</td>
<td>582 s, 0.8–7.6 m</td>
</tr>
<tr>
<td></td>
<td>1600, 1500 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>1705 s</td>
<td>224 (4,12), 255sh (3.91)</td>
<td>5.56 d (11), 7.0–7.7 m</td>
</tr>
<tr>
<td></td>
<td>1455, 1500 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>1730 s</td>
<td>224 (3,96), 255sh (3.81)</td>
<td>5.57 d (15.5), 7.0–7.7 m</td>
</tr>
<tr>
<td></td>
<td>1465, 1500 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In the UV spectra the abbreviation "sh" indicates shoulder. Intensities in the IR spectra: s is strong, w is weak, and the remaining bands are of medium intensity. A doublet signal at ~122 ppm (with respect to C₆F₆) with JHF ~ 15 Hz is observed in the ¹⁹F NMR spectra of X and XI.

TABLE 2. Rate Constants for the Isomerization of Aziridines II–VI [k·10⁻⁵, sec⁻¹ (temp., °C)]*

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR spectroscopy</th>
<th>PMR spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>2.20 (95), 17.2 (115), 42.9 (125)</td>
<td>56.1±2.1 (110)</td>
</tr>
<tr>
<td>III</td>
<td>5.67 (95), 27.5 (115), 64.9 (125)</td>
<td>32.2±1.9 (115)</td>
</tr>
<tr>
<td>IV</td>
<td>37.4±0.10 (95), 15.8±0.3 (95), 62.7±1.8 (110)</td>
<td>79.8±4.5 (115)</td>
</tr>
<tr>
<td>V</td>
<td>2.97±0.49 (30), 12.3±0.8 (45), 61.2±3.5 (60)</td>
<td>22.5±0.8 (50), 21.9±0.9 (95)</td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td>10.8±0.8 (45), 13.3±0.8 (45)</td>
</tr>
</tbody>
</table>

*The aziridine concentration in solution in the determination by IR spectroscopy was 1.7%, as compared with ~10% in the case of determination by PMR spectroscopy; A) determined from the aziridine consumption, B) determined from the imidoyl halide accumulation. †The rate constants were presented in [5]. ‡For a mixture containing 60% aziridine III and 40% aziridine IV.

TABLE 3. Kinetic Parameters of the Isomerization of 3,3-Dihalo-1,2-diphenylaziridines (at 100°C)

<table>
<thead>
<tr>
<th>Compound</th>
<th>k, sec⁻¹</th>
<th>krel</th>
<th>ΔH°, kJ/mole</th>
<th>ΔS°, J/deg-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>I*</td>
<td>5.85·10⁻⁴</td>
<td>1</td>
<td>106±1</td>
<td>−62±3</td>
</tr>
<tr>
<td>II</td>
<td>1.52·10⁻⁴</td>
<td>35.8</td>
<td>108±4</td>
<td>−30±11</td>
</tr>
<tr>
<td>III</td>
<td>3.78·10⁻⁴</td>
<td>6.4</td>
<td>117±2</td>
<td>−18±5</td>
</tr>
<tr>
<td>IV</td>
<td>8.56·10⁻⁵</td>
<td>14.5</td>
<td>95±4</td>
<td>−70±10</td>
</tr>
<tr>
<td>V</td>
<td>2.51·10⁻⁴</td>
<td>43.1</td>
<td>104±4</td>
<td>−37±2</td>
</tr>
<tr>
<td>VI</td>
<td>1.51·10⁻²</td>
<td>2560</td>
<td>81±5</td>
<td>−64±17</td>
</tr>
</tbody>
</table>

*Taken from [5].