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Aziridines. XII. Kinetics of the Isomerization of 1-*p*-Nitrobenzoyl-2,2-dimethylaziridine (I).

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Previous evidence supports the view that the thermal isomerization of suitably substituted 1-acylaziridines to give unsaturated amides occurs via a cyclic transition state such as II (2) and therefore may be classified among the well-known group of pyrolytic *cis*-eliminations (3). Such a reaction would be expected to be unimolecular and kinetically of the first order. We have now found that the rearrangement of 1-*p*-nitrobenzoyl-2,2-dimethylaziridine (I) to *N*-(β -methallyl)-1-*p*-nitrobenzamide (III) in bis-(2-methoxyethyl)ether (diglyme) is a first order reaction at 72, 86 and 101°.

The course of the reaction was readily observed by measurement of the NH band of III in the infrared absorption spectrum. The results of a typical kinetic run are presented graphically in Fig. 1, showing excellent agreement with the first-order rate equation. Kinetic runs at three different initial concentrations gave similar values for the first-order rate constant, as summarized in Table 1. The effect of change in temperature was studied by conducting kinetic runs at 72, 86 and 101°, as presented in Table 1.

TABLE 1

Isomerization of I in Diglyme. Effect of Change of Initial Concentration on Rate Constant at 101° and Effect of Change of Temperature on Rate Constant at Initial Concentration of 0.250 M.

Temperature °C	Initial Conc., M	k, min. ⁻¹ (graphical)
101.1	0.475	1.08 x 10 ⁻²
-	0.475	1.04 x 10 ⁻²
-	0.100	1.24 x 10 ⁻²
-	0.100	1.02 x 10 ⁻²
-	0.250	1.09 x 10 ⁻²
-	0.250	1.09 x 10 ⁻²
-	0.250	1.11 x 10 ⁻²
72.4	0.250	6.9 x 10 ⁻⁴
-	0.250	6.4 x 10 ⁻⁴
-	0.250	5.8 x 10 ⁻⁴
86.1	0.250	2.64 x 10 ⁻³
-	0.250	2.56 x 10 ⁻³
-	0.250	2.66 x 10 ⁻³

These data were used in the conventional manner (4) for the calculation of the activation energy, the frequency factor and the entropy of activation (at 86°). The graphical representation of the temperature dependence is shown in Fig. 2.

A comparison of these parameters with data reported for other typical unimolecular pyrolytic *cis*-eliminations is presented in Table 2. The results are in agreement with the formulation of the reaction as a concerted, cyclic process. In particular, the large negative entropy of activation is in accord with a highly ordered transition state II.

TABLE 2

Activation Parameters for Some
Pyrolytic *cis*-Eliminations (3).

Compound	Experi- mental Activation Energy Kcal moles ⁻¹	Fre- quency Factor 10 ⁻¹² A	Entropy of Activation - Δ S* e. u.
Isopropyl acetate	45.0	10	
Cholesteryl acetate	44.1	3.1	3.5
Cholesteryl S-methyl xanthate	32.9	2.4	4.7
Compound I	25.2	5.8	10.4 \pm 1.9

EXPERIMENTAL (5)

1-*p*-Nitrobenzoyl-2,2-dimethylaziridine (I) and *N*-(β -Methallyl)-*p*-nitrobenzamide (III) were prepared as previously described (6). Bis-(2-methoxyethyl)ether (diglyme) was refluxed over sodium metal for a day followed by distillation, b.p. 161-163°.

For the kinetic studies, approximately 0.25 ml. samples of the solutions of I in diglyme were sealed in Kimax Neutraglas ampules and placed in a thermostat. About ten ampules were prepared for each run. At appropriate intervals, ampules were withdrawn and kept on ice for analysis.

The course of the reaction was followed by measuring the height of the NH band in the infrared absorption spectrum at 3370 cm⁻¹. This value was found to be a linear function of the concentration of III in diglyme in the range 0-0.250 M. The concentration of I was calculated by subtracting the measured concentration of III from the initial concentration of I. Solutions for the construction of a calibration curve were prepared by mixing measured volumes of I and III such that the total concentrations of the two species was equal to the initial concentration of I in the solution used for the kinetic experiments. For the kinetic studies at 0.100 M initial concentration, 0.182 mm sodium chloride cells were used; 0.092 mm cells were used for the two higher concentrations.

Because of insufficient solubility of III, the analytical method failed above concentrations of 0.250 M. Therefore the kinetic runs at initial concentrations of 0.475 M were carried out only to approximately half-time.

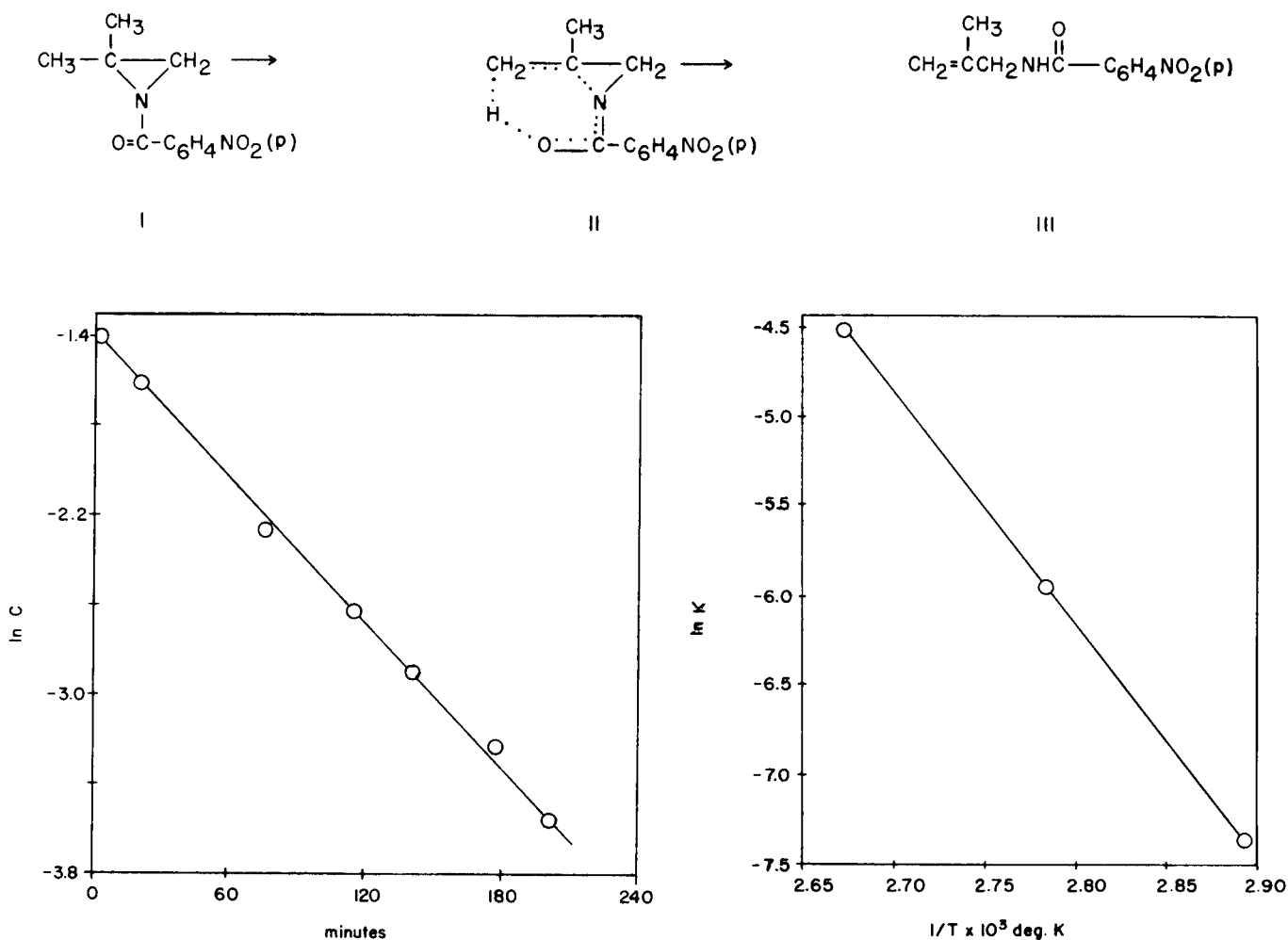


Figure 1
Sample first-order plot for isomerization of I to III. Initial concentration 0.250 M I in diglyme solution, temperature 101.0°C.

Figure 2
Graphic presentation of Arrhenius Equation for the determination of experimental activation energy.

For each kinetic run the rate constant was calculated both numerically and graphically. The two methods were in agreement and only the values obtained graphically are given in Table 2.

REFERENCES

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