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# A Kinetic Contribution to the Knowledge of Carbon-rings

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A mechanism involving a cyclic intermediate has been suggested by Welsh and Fodor independently. To obtain a deeper insight acyl shifts with (1) 2-acylamidocyclopentanol-*cis* (2) 2-benzamidocyclohexanol-*cis* and (3) *trans* have been investigated kinetically with hydrochloric acid in dry dioxan.

Measurements were performed with (1) at 25° etc., with (2) and (3) 70—90°C. Methods: (a) back titration of excess hydrochloric acid (b) determination of amino-groups liberated by acyl shift. With compounds (2) and (3) both methods proved useful, with (1) excess hydrochloric acid could not be titrated, for excess alkali resulted in reverse rearrangement of the aminoester-base.

The order of reaction was established from initial and half-time reaction-rate employing $x/t$ diagram. The quotient of half-time and quarter-time, as derived from second-order equation is consistent with experimental data, while reaction rate constants calculated from initial reaction rates are 1.

Activation energies were calculated: for (1) 12.89 Kcal/mol, (2) 15.02 Kcal/mol, (3) 17,21 Kcal/mol. In case of 2-benzamidocyclopentanol-*cis* only energy requirement of acyl shift seems involved. In the *cis*-cyclohexanolamine (2) transitory ring formation can occur in both (*e, a* and *a, e*) positions of the groups concerned, while benzamido-cyclohexanol *trans* has a single conformation of the ring (*e, e*-position of functional groups) enabling collision necessary to ring formation. Accordingly, the *trans* derivative has half as specific rate as (2); activation energy of *trans* form is higher.

Thermodynamic potentials of cyclohexanol derivatives differ markedly from that of the cyclopentylamine (24 Kcal/mol against 20 Kcal/mol). This may be considered as an effect of the vibrational changes of cyclohexane skeleton which results in a noteworthy decrease in the probability of intramolecular collisions.

## INTRODUCTION

Nature, particularly in plants, produces a great variety of organic alicyclic compounds (e. g. terpenes, steroids, resin acids). Owing to the considerable interest adherent to a number of them the determination of their structure deserved paramount interest.

There was no lack as to the twenties concerning this trend, however, the first modern treatment of the problem of ring formation and ring stability of such systems has to be attributed to L. Ruzicka.[1] The series of papers »Zur Kenntnis des Kohlenstoffringes« which has been started by him in 1926, reached nowadays part 72, as being continued by professor V. Prelog.

The importance of Part VI. of this series »Über die relative Bindungsleichtigkeit, die relative Beständigkeit und den räumlichen Bau der gesättigten Kohlenstoffringe« stands at its own merits by considering first these problems in terms of thermodynamics, kinetics and probability factors.

Alicyclic chemistry is now at its highlight. The concept of *equatorial* and *axial* bonds, propounded by Hassel[2] has been developed by Barton[3] and his school to »conformational analysis«, one of the most fruitful theories in organic chemistry.

## AIM AND SCOPE OF THIS PAPER

The modest results we may outline at this opportunity involve a kinetic investigation of acyl migrations in some acylated amino alcohols having cyclopentane and cyclohexane skeleton. Our endeaveour was to elucidate the role of the flexible cyclohexane skeleton in acyl migration as compared with the course of the same reaction in a related though rigid system. In other terms: acyl migration of 2-amino cyclohexanols can take place only with neighbouring groups through the formation of cyclic intermediates. Therefore we intended to determine activation energies of this process which comprises the energy requirement for the interconversion of chair conformations and hereby of the bonding of the groups (*a, a* $\rightarrow$ *e, e* and *a, e* $\rightleftarrows$ *e, a,* resp.) concerned as well. On the other hand, 2-amino-cyclopentanols have the reactive groups in a performed state, *i. e.* near placed, so acyl migration ought not be anticipated by any change in the ring system. Consequently, comparison of activation energies of the six-membered, *cis-* and *trans* 2-acylamino alcohols with that of the five-membered system was expected to give informations of interest as to the energy required by the interconversion of the conformations of the cyclohexane ring.

Hence, acyl migration may serve as a tracer in revealing energy changes in flexible, first in cyclohexane systems.

In order to evaluate the contribution of steric factors, some of the kinetic data recorded for other, arylaliphatic and alicyclic amino alcohols will be dealt with.

## STEREOSPECIFICITY AND R-MECHANISM OF ACYL MIGRATIONS *N* $\rightleftarrows$ *O*

The rearrangement of 2-acylamido-alcohols into the salts of *O*-acyl-2-amino alcohols by the action of acids and the reversibility of this process initiated by alkali has been recorded at an early date. Although an intramolecular mechanism has been suggested by Bergmann[4], Phillips and Baltzly[4], Bruckner,[4] Welsh and Fodor and Kiss[4], the steric requirements, *i. e.* the stereospecificity of this reaction, was first recognised by this team[5].

*Cis*-2-amino alcohols underwent *N* $\rightarrow$ *O* acyl migration reversibely (it is to be noted the reverse *O* $\rightarrow$ *N* shift as occuring invariably with retention of configuration) *i. e.* with retention and faster than their *trans*-epimers. Furthermore some *trans* derivatives — except those having a cyclohexane skeleton — suffer Walden inversion at the hydroxyl-bearing carbon atom, which makes the process irreversible. Hence this marked selectivity gave informations as to the steric structure of several epimeric pairs of 2-amino alcohols. Accordingly, a new method in determining the configurations of 2-amino

alcohols has been based upon[5]. In addition it enabled us to elucidate the stereochemistry of some esocyclic 3-amino alcohols, particularly of tropanols[6], granatanols and so.

The retention (R) mechanism of $N \rightarrow O$ shifts may be envisaged as follows (Fig. 1). The carbonyl-*N*-bond is weakened by the electrophilic attack of a proton (or hydrogen chloride), on the carbonyl-oxygen followed by a nucleophilic action exerted by the neighbouring hydroxyl-oxygen upon the carbonyl carbon atom giving rise to the formation of a transition state, expressed in terms of covalent bonds as an orthoacid-monoester-monoamide. This latter may be decomposed, in turn, with breaking down of the C—N bond and further — perhaps tautomeric — protonation of the amino nitrogen to form an ester-ammonium salt.

The reverse process, $O \rightarrow N$ migration, seems to be initiated by a nucleophilic attack of the nitrogen in the free aminoester base on the electrophilic ester carbonyl-carbon atom leading to a similar transition state as suggested for $N \rightarrow O$ shift, except it is not protonated. The cleavage of the latter into the acylamide seems to take place spontaneously.

This concept is supported by several experimental findings *inter alia* by the synthesis and study of the mixed magnesium salt of an μ-hydroxy oxazolidine[5].

## EARLIER KINETIC INVESTIGATIONS ON ACYL MIGRATIONS

Unfortunately, however, so far kinetic investigation of this process has been performed but in few cases. The course of acyl migrations was pursued (1) by estimating the consumption of hydrochloric acid by the hydroxy amide. It may be taken into consideration that the ester-ammonium salt is neutral to methyl red while the acylamide salt formed primarily titrates as »free« hydrochloric acid. Accordingly, Welsh[7] treated each *N*-acyl ephedrine epimer with 12% excess hydrochloric acid in 96% ethanol at 30° C with subsequent back titration of the excess acid. The *k*-values calculated on the basis of second order reaction rate equation amounted to $8.2 \cdot 10^{-1}$ mole/liter/hour or, in the customary manner: $1.36 \cdot 10^{-2}$ mol/liter min. (2). A second series of measurements was carried out by Mc Casland[8] who estimated the increase of the substance containing primary amino-nitrogen (*i. e.* of the amino ester salt formed) during $N \rightarrow O$ acyl shift, making use of the van Slyke method. On comparing the rate of rearrangement for *cis* and *trans* 2-acetamino-cyclohexanols with that of epimeric *N*-acetyl-inosamines in 0.08 molar concentration in water 25° *k*-values of $8.7 \cdot 10^{-5}$ and $1.4 \cdot 10^{-5}$ mol/liter min. for the *cis* and *trans* modification respectively, of the former pair have been recorded.

The three great-order discrepancy between reaction rates of arylaliphatic and alicyclic types seems rather surprising. This points to the predominant role of structural factors as to the speed of acyl migration even of the *cis*-derivatives apart from differences inherent in the various methods used.

## RECENT INVESTIGATIONS

In order to obtain quantitative information as to the activation energy and entropy as well as the thermodynamic potential of the activation of $N \rightarrow O$ acyl migrations involving R mechanism, the rearrangement of *cis N*-

benzoyl and *O*-benzoyl-2-aminocyclopentan-1-ol has been chosen first, having two rigidly linked neighbouring functional groups »purely« *cis* placed, which should preclude any change of conformation, so no other contribution to the energy requirements of this process could be expected. Subsequently, similar data arising from measurements on epimeric *cis* and *trans* 2-amino-cyclo-

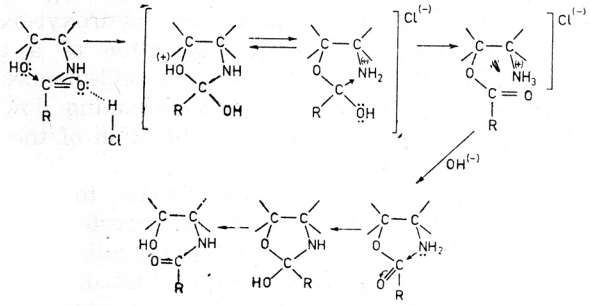


Fig. 1.

hexan-1-ols will be discussed. As the third item, acyl shift in *cis* 4-acylamino cyclohexan-1-ol is intended to be investigated as a model, for here acyl migration can only occur in the boat conformation of the ring so data of interest concerning the transition of chair into boat conformation of this system may be obtained.

(a) *Rearrangement of* cis-*2-benzoyloxy cyclopentylamine into* cis N-*benzoyl-2-amino-cyclopentan-1-ol.*

The first attempt to titrate back excess hydrogen chloride besides *O*-benzoyl and *O*-*p*-nitrobenzoyl-2-amino-cyclopentanol hydrochloride respectively which formed by acyl migration $N \rightarrow O$ (as it occured with the ephedrines and amino cyclohexanols), however, failed, since the first drop of excess alkali induces immediately a reverse, *i. e.* $O \rightarrow N$ acyl migration so the total hydrogen chloride (free and bound together) should be determined only.

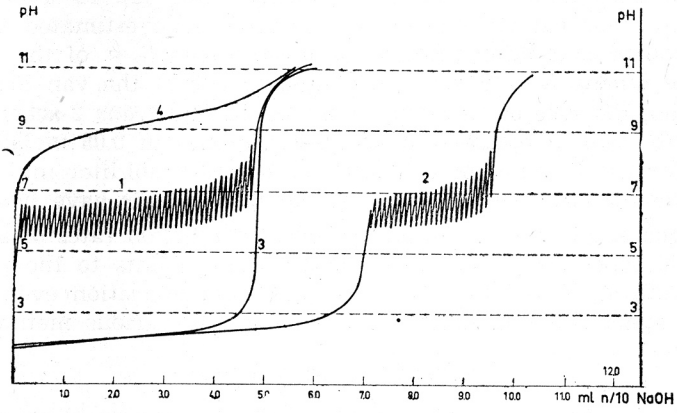



Fig. 2. Curve 1: DL-*cis* 2-Aminocyclopentylbenzoate. HCl 0.0005 *N* in 30 ml. water.
Curve 2: DL-*cis* 2-Aminocyclopentylbenzoate, HCl 0.0005 *N*+5 ml. 0.1 *N* HCl in 30 ml. water.
Curve 3: 5 ml. 0.1 *N* HCl in 30 ml. water.
Curve 4: 0.0005 *N* $NH_4Cl$ in 30 ml. water.

It seemed worthwile to follow this rearrangement potentiometrically. To an aqueous solution of (*O-p*-nitrobenzoyl-2-hydroxycyclopentyl)-ammonium chloride *N*/10 sodium hydroxide has been added drop by drop (0.02 ml. each) resulting in an instantaneous increase of potential values as indicated by the swing of the needle of the voltmeter which returned then into the ground state within, 10—15 minutes. This phenomenon could be observed invariably, until the stoichiometric amount of alkali has been added to. After this point has been reached the curve takes the shape of that of a normal acidimetric titration (Fig. 2). For sake of comparison the titration of *N*/10 hydrochloric acid with *N*/10 sodium hydroxide is depicted (curve 3), while curve no. 2 shows titration of 5 ml. *N*/10 hydrochloric acid in the presence of the same benzoyloxycyclopentyl ammonium chloride as in experiment no. 1. The titration of ammonium chloride with *N*/10 sodium hydroxide is envisaged by curve no. 4.

The rise of potential indicates that the substituted amino ester *base* has been liberated which, in turn, disappears at a measurable rate as shown by the continuous decrease of this value. This fact may be attributed to steric factors in $O \rightarrow N$ shifts, since neither *cis* nor *trans* 2-benzoxy-cyclohexyl ammonium chloride does affect titration of excess hydrogen chloride. In other terms: 2-aminocyclopentylbenzoate rearranges faster than either *cis* or *trans* 2-aminocyclohexyl benzoates, owing to the steric proximity of the functional groups.

(b) $N \rightarrow O$ *acyl shift in* cis-2-*benzamidocyclopentan-1-ol.*

This observation may serve as a basis in determining rate order and activation energy of acyl migrations $O \rightarrow N$, however, for our present aim (*i. e.* to investigate $N \rightarrow O$ migrations) we were bound to turn to the method outlined by Mc Casland involving estimation of the amino ester formed, by the amino nitrogen determinations we performed in micro scale according to Hussey and Maurer[9]. The end product of $N \rightarrow O$ acyl shift was found to give higher $NH_2$ values (107.44%) in accordance with other alicyclic amino alcohols which has been taken into correction during the kinetic measurements.[10]

These have been conducted in dioxan instead of water to avoid side reactions, *e. g.* ester hydrolysis. Unfortunately, however, several difficulties of theoretical and practical kind emerged, for (1) the relationship between concentration and activity *i. e.* activity coefficient of hydrogen chloride is not known, accordingly we were bound to calculate reaction rate constants from concentration data only. (2) In this solvent undissociated HCl dipoles may be present according to dipole moment date by Weith[11] and, in addition, by conductometric measurements carried out in this Laboratory which furnished extremely low (resistance greater than 100.000 Ω) conductivity values. (3) The greatest difficulty encountered arises from the fact that the absolute absence of water in dioxan can only be secured on cheking by the K. Fischer method, which, however, does not enable the detection of traces of water after dioxan has been saturated with HCl.

Hydrogen chloride has been taken in a ten-thirty fold excess which rendered the reaction to be completed within a few hours corresponding to a conversion of 82—85%. Measurements have been carried out within the range of 12—42° at four different temperatures.

Reaction rate constants have been calculated according to the integrated form of second-order equation. Activation energies ($\Delta H^{\ddagger}$) were calculated from the Arrhenius plot, while the entropy ($\Delta S^{\ddagger}$) and the thermodynamic potential ($\Delta G^{\ddagger}$) of activation arise from the following equations:

$$\Delta S^{\ddagger} = 4.574 \left( \log k + \frac{\Delta H^{\ddagger}}{4.574\, T} - \log \frac{kT}{h} \right)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

TABLE I

| $10^3/T$ | Log · $k$ + 3 | $\Delta H^{\ddagger}$Kcal/mol | $\Delta S^{\ddagger}$Kcal/mol | $\Delta G^{\ddagger}$ Kcal/mol |
|---|---|---|---|---|
| 3,515 | 0.64836 | | —0.0240 | 19.729 |
| 3,388 | 1.02119 | | —0.0239 | 19.938 |
| 3.277 | 1.31806 | 12.892 | —0.0240 | 20.218 |
| 3.173 | 1.06314 | | —0.0244 | 20.577 |

(c) *Rearrangement of* (±) cis *and* trans *2-benzamido-cyclohexan-1-ols into the epimeric 2-benzoyloxy-cyclohexyl-ammonium-chlorides*

Acyl shift occors in both cases reversibely and with retention of configuration. Both the consumption of hydrogen chloride by the hydroxyamide and the amount of the end product which formed by acyl shift have been determined, to check wether the whole amount of HCl has been used by the molecule for the conversion of hydroxy amide into the hydrochloride of the amino ester.

For this purpose measurements of reaction rates by method (1) have been performed in an interval of 71—91° at five different temperatures in dry dioxan. Since dioxan itself is acidolysed slowly by hydrogen chloride at higher temperature, this consumption of HCl has been measured at each temperature and concentration and taken into correction as »blind value«. The highest rate of the side reaction is $k = 10^{-4}$ while that of acyl migration amounts to $k = 10^{-2}$. Notwithstanding other solvents might have caused difficulties of similar kind as well.

The solution has been prepared by dissolving the compound in dry dioxan containing excess hydrogen chloride. The compound showed solubilities strikingly greater in dioxanic hydrogen chloride than in the pure solvent, *e. g.* the *trans* derivative is soluble to 1% at 20°C in dioxan whereas 10 *N* HCl in dioxan may solve 8% of it and in 2*N* HCl in dioxan a concentration of 11% has been reached.

This points to chemical bonding of HCl expressed in terms of an acylamide salt, which takes place immediately after the substrate became dissolved.

The presence of the latter, however, could not be revealed by our measurements by any change in conductivity, owing to the extremely low rates of both HCl in anhydrous dioxan and of the compound dissolved therein.

Should we suggest the formation of acylamide salt to occur instantaneously in the cold then its subsequent rearrangement is expected to obey a first-order reaction. However, the first-order constants indicate decrease

with time and show a marked variation with the concentration of HCl. Accordingly, this concept cannot be taken any more for granted. The reaction rate constants calculated on the basis of bimolecular equations are in better agreement though they point to a more complex course than bimolecular.

Using method (2) *i. e.* performing amino nitrogen determinations at three different temperatures, reaction rate constants have been found in fairly good agreement with those obtained by method (1), *i. e.* by alkalimetric titration. Activation energies, entropies and thermodynamic potentials of activation are shown in Table II.

TABLE II

(±)cis-2-*Benzamido-cyclohexan*-1-*ol*

| Method | $10^3/T$ | log $k+3$ | $\Delta H^{\ddagger}$Kcal/Mol | $\Delta S^{\ddagger}$*Kcal/Mol* | $\Delta G^{\ddagger}$*Kcal/Mol* |
|---|---|---|---|---|---|
| (1)Alkalimetric titration | 2.746 | 1.31387 | | —0.0254 | 24.26 |
| | 2.784 | 1.20140 | | —0.0253 | 24.10 |
| | 2.824 | 1.06818 | 15.02 | —0.0253 | 23.97 |
| | 2.863 | 0.95809 | | —0.0251 | 23.80 |
| | 2.906 | 0.81425 | | —0.0251 | 23.67 |
| (2) Amino nitrogen determination | 2.746 | 1·51455 | | —0.0224 | 23.96 |
| | 2.824 | 1.25527 | 15.78 | —0.0223 | 23.66 |
| | 2.906 | 0.96332 | | —0.0223 | 23.45 |
| (±)trans-2-*Benzamido-cyclohexan*-1-*ol* | | | | | |
| (1)Alkalimetric titration | 2.746 | 1.14489 | | —0.0201 | 24·54 |
| | 2.784 | 0.97772 | | —0.0202 | 24.47 |
| | 2.824 | 0.83059 | 17.21 | —0.0202 | 24.35 |
| | 2·863 | 0.71265 | | —0.0200 | 24.19 |
| | 2.906 | 0.55509 | | —0.0200 | 24.08 |
| (2) Amino nitrogen determination | 2.746 | 1.14799 | | —0.0169 | 24.60 |
| | 2.824 | 0.85733 | 18.39 | —0.0167 | 24.30 |
| | 2.906 | 0.50515 | | —0.0168 | 24.14 |

## DISCUSSION

There are several difficulties in comparing reaction rates of other authors measured with different amino alcohol models, for (1) both acetyl and benzoyl derivatives have been used (2) water, alcohol and dioxan have been adopted as solvents, and (3) measurements have been performed within quite different temperature ranges.

Notwithstanding, extrapolation of these data to the same range of temperature allows to estimate great-order of reaction rates semiquantitatively which seems to be still instructive (Table III).

(1) It is obvious that the structure of the carbon skeleton controls the reaction rate of acyl shifts rather than either the migrating group, or the solvent used. The proportion of rates in arylaliphatic: cyclopentane: cyclohexane derivatives takes: 100:100:2 and in the inosamines even 0.1.

(2) Within an epimeric pair acyl-shift occurs according to R-mechanism 4—6 times faster in the *cis*-modification that in the *trans* one. However, in the aryl-alkyl derivative (*N*-benzoyl ephedrine) this proportion is still greater

TABLE III

| Compounds | $T$ | $k \cdot 10^6$ Mol/l. min. | $\Delta H^{\ddagger}$ | $\Delta G^{\ddagger}$ | $k \cdot 10^6$ extrapolated to 298° K | $\Delta G^{\ddagger}$ |
|---|---|---|---|---|---|---|
| *N*-Benzoyl-ephedrine[7] | 303 | 13600 | | | 13600 | |
| *cis*- 2-Benzamido-cyclopentan-1-ol | 303 | 21300 | 12.9 | 20.2 | 12900 | 20.00 |
| *cis*- 2-Benzamido-cyclohexan-1-ol | 354 | 12000 | 15.2 | 24.0 | 302 | 22.57 |
| *trans*-2-Benzamido-cyclohexan-1-ol | 354 | 6800 | 17.2 | 24.3 | 76 | 23.05 |
| *cis*- 2-Acetamido-cyclohexan-1-ol[8] | 298 | 88 | | | 88 | |
| *trans*- 2-Acetamido-cyclohexan-1-ol[8] | 298 | 14 | | | 14 | |
| *cis*-2-*N*-acetyl-inosamine[8] | 299 | 12 | | | 12 | |
| *trans*- 2-*N*-acetyl-inosamine[8] | 299 | 3 | | | 3 | |

while with *trans*-2-benzamido-cyclopentanol no comparison can be made owing to the impossibility of an R-mechanism, for here during acyl migration inversion takes places.

(3) The marked discrepancy in the speed of acyl migration in the cyclohexane series as contrasted with the cyclopentane derivative can be attributed to the special stereochemical features only, *i. e.* to the flexibility of the non-coplanar ring system.

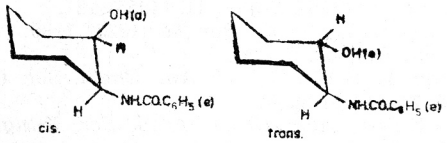
Our own measurements enabled us to give a more detailed picture as to the energy changes accompanying this process which supports the following interpretation.

$G^{\ddagger}$ values are closely related for the rearrangement of *cis* and *trans* cyclohexanolamine derivatives; they differ by 0.3 kcal only while it is by 2.6 kcal/mole lower for the cyclopentanolamine. It has been kept in mind that $\Delta G^{\ddagger}$ values show a low dependence on temperature, on the other hand *cis* benzamidocyclopentanol reacts at a lower temperature than the benzamido cyclohexanols. In consequence, thermodynamic potential values belonging to identical temperature-obtained by extrapolation- have been compared.

$\Delta G^{\ddagger}$ values reflect the stability of transition states hence the continuous interconversion (*i. e.* transvibration) of different conformations of the cyclohexane skeleton seem to be responsible for both essentially lower rates and for the greater thermodynamic potential of activation.

In terms of conformational analysis, however, one might object to this concept the different chair forms of the cyclohexane ring in the two epimers as being not equivalent, for the following preferred conformations can be

predicted for the *cis* and *trans* derivative, respectively, both having the bulky benzamido group in an *equatorial* position. Accordingly, the probability for interconversion of conformations is expected to be not too great.




However, according to Hassel[2] in several ortho disubstituted cyclohexanes the interference of bulky neighbouring groups may act in such a manner that they assume d i a x i a l position despite this is energetically less favoured. Consequently there is no reason to preclude transvibration in the cyclohexane skeleton the more so, since it is indicated by the increase in both activation energy and $G^{\ddagger}$ values.

(4) Furthermore, considerable difference is to be observed between activation energies required for acyl shift of the *cis* and of *trans* *N*-benzoyl-cyclohexanolamines. Taking into consideration that the *cis* derivative may undergo activation in b o t h conformations of the ring, *i. e.* possessing the functional group either in *e, a* or in *a, e* position, while the *trans*-acylamino alcohol can enter ring closure with d i e q u a t o r i a l l y placed groups only, one may conclude that the higher energy requirement for the *trans* derivative is predetermined by its steric structure.

However, it may be argued against this concept the *trans* derivative as being more stable than its epimer, consequently the energy to reach the peak of the activated state must be greater for the former one. In order to give this objection positive or negative response, the heat of combustion will be determined for both compounds as well as for the corresponding amino-ester salts. In addition, solvation heats arising from dissolving the hydroxyamides in dioxanic HCl ought to be established.

The discrepancy of r e a c t i o n r a t e s between the rearrangement in *cis* and *trans* derivatives points to the presence of b o t h conformations possible in the latter molecule.

(5) It is hard to give due consideration to the extremely low migratory aptitude of the acetyl inosamine epimers. The same vibrational factors we made responsible in case of the simpler cyclohexane derivatives might prevail here to a smaller extent, for an a l l - e q u a t o r i a l conformation of the *trans* derivative and a p e n t a - e q u a t o r i a l - m o n o - a x i a l orientation of the *cis* one must predominate. However, hydrogen bonding of the hydroxyl groups to reach other might decrease the probability of the hydroxyls adjacent to the acetamino roup, in acting as nucleophiles upon the carbonyl-carbon atom.

## CONCLUSION

This study may be regarded as a first kinetic approach to the contribution of energy in the cyclohexane system to this intramolecular reaction. The statements we made should be supported by further kinetic, calorimetric and spectroscopic investigations in the near future.

Full details of the experimental work will be published in *Tetrahedron.*

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## IZVOD

### Kinetički prilog poznavanju ugljikovih prstena

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Opisano je kinetičko ispitivanje acil migracija kod nekih aciliranih amino alkohola, koji sadrže ciklopentanski i cikloheksanski prsten. Welsh i Fodor su nezavisno predložili mehanizam reakcije acil migracija pretpostavljajući jedan ciklički međuprodukt. Radi boljeg upoznavanja reakcije kinetički su ispitani acilni pomaci (1) *cis*-2-acilamidociklopentanola, (2) i (3) *cis*- i *trans*-2-benzamidocikloheksanola sa solnom kiselinom u suhom dioksanu.

Određen je stepen reakcije i izračunate su energije aktiviranja: za (1) 12.89 Kcal/*Mol.*, za (2) 15.02 Kcal/*Mol.* i za (3) 17.21 Kcal/*Mol.*

Ovi radovi i isiptivanja predstavljaju prvi kinetički pokušaj proučavanja doprinosa energije cikloheksanskog sistema u jednoj intramolekularnoj reakciji.

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