

A Proposal for a Branching Mechanism in Medium-sized Cycloalkanes: MINDO/3 Study of the Hypersurface for Isomerization of Cyclohexylium to 1-Methylcyclopentylum Ion

Pedro M. Viruela-Martín, Ignacio Nebot,* Rafael Viruela-Martín, and Josep Planelles
 Departamento de Química-Física, Facultad de Química, Universidad de Valencia, Burjassot, Valencia, Spain

A MINDO/3 study on the branching rearrangement mechanism for cycloalkanes is presented. Starting from cyclohexylium ion, a reaction path to methylcyclopentylum ion is found. Two different intermediates and several alternative transition states are localized, and then characterized by hessian diagonalization after complete optimization of geometry. The barrier height calculated for the inverse path (methylcyclopentylum to cyclohexylium) (21.7 kcal mol⁻¹) agrees well with the unique available experimental datum (17 kcal mol⁻¹) in the range of applicability of the MINDO/3 method. The mechanism proposed is consistent with the empirical mechanism suggested by Brouwer for branching rearrangement of linear alkanes.

Catalytic isomerization, cracking, and dehydrogenation of hydrocarbons play an important role in chemistry of petroleum. Zeolites are the most active solid acid catalyst for these reactions^{1,2} and their activities can be modified after exchange with various cations.¹⁻⁴ In spite of earlier evidence,¹⁻⁴ Corma⁵ and Minachev⁶ have recently found that acid forms of zeolite show great activity in reactions of saturated hydrocarbons even when no exchange with transition metal cations has taken place.

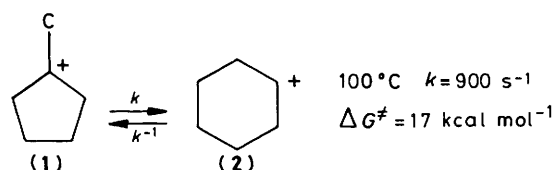
It is now well established^{1,7-9} that reactions on acid surfaces proceed *via* carbenium ions. It is generally assumed that such reaction mechanisms are valid for heterogeneous reactions on solid acid catalysts,⁷⁻¹⁰ as well as for reactions in a homogeneous phase (superacid catalysts).¹¹

The mechanism for alkane isomerization reactions involves (1) hydrogen transfer to give an alkylum ion, and (2) rearrangement of this intermediate carbenium ion. The latter step may include a series of elementary processes involving alternative rearrangement and hydrogen-transfer reactions, until the carbenium ion is destroyed. It is assumed that carbenium ion rearrangement is the slowest step, unless the initial hydrocarbon has no tertiary carbon atom; in this case, the slowest step will be hydrogen transfer.

Rearrangements may be classified¹² as (a) non-branching, in which the mechanism involves 1,2-alkyl and/or 1,2-hydrogen shifts (in agreement with experimental results,^{12,13}) and (b) branching, where it is assumed that the mechanism involves an intermediate such as a protonated cyclopropane;¹² for branching rearrangements the 1,2-alkyl and/or 1,2-hydrogen shift mechanism is discarded since it should lead to higher activation energies^{12,13} resulting from the presence of primary carbenium ions.

We present here a theoretical study of the branching rearrangement of cyclohexane. When cyclohexane flows through a solid acid catalyst^{6a} such as mordenite (containing no transition metals), isomerization to methylcyclopentane takes place along with other reactions. Isomerization of cyclohexane to methylcyclopentane takes place also in the homogeneous phase in the presence of superacid catalysts;^{14,15} the equilibrium mixture at 25 °C is composed of 23% of methylcyclopentane and 77% of cyclohexane. However, the tertiary 1-methylcyclopentylum ion (1) is more stable than the secondary cyclohexylium ion (2) by 6–10 kcal mol⁻¹,^{15,16} the estimated activation energy for the isomerization (1) → (2) being about 17 kcal mol⁻¹.^{12b}

We have chosen this reaction for two reasons: (a) it serves as a starting point and a model for the isomerization of



methylcyclohexane to 1,3- and 1,2-dimethylcyclopentane and ethylcyclopentane, important processes in the petroleum industry;⁷ and (b) there are more experimental data relating to the isomerization of cyclohexane than of methylcyclopentane, and we are concerned with the correlation between theoretical results and the general empirical mechanism suggested for branching rearrangements by Brouwer.¹²

Methodology.—The theoretical model for the isomerization of cyclohexane to methylcyclopentane has been studied by the MINDO/3 method;¹⁷ this method has been shown to be useful for studying classical as well as non-classical carbocations, particularly in calculating heats of formation and relative energies in the gas phase.¹⁸ Thus MINDO/3 is well adapted to study chemical reactions of hydrocarbons.^{18,19} Moreover, since it is a semiempirical method, total optimization of the geometry at each position on the reaction co-ordinate is feasible, whereas this would be impracticable at an *ab initio* level.

As the MINDO/3 parametrization has been chosen to reproduce hydrocarbon experimental heats of formation, the results obtained from the calculations on pure hydrocarbon carbenium ions by MINDO/3 are as good as those obtained by *ab initio* methods in some cases, even when large basis sets are used, and including the calculation of electronic correlation energy.^{20,21}

We have carried out the calculation of the minimum-energy reaction path (MERP)²² for the isomerization of cyclohexylium (2) to 1-methylcyclopentylum ion (1), by defining the geometrical parameters related to the reaction co-ordinate, and optimizing all the other geometrical parameters at each point on the MERP, by means of the metric variable Rinaldi procedure.²³ All the calculations were performed with an updated version of the program system GEOMO.²⁴ The geometries were fully optimized by the Rinaldi algorithm, and with a gradient norm threshold of 10⁻⁶ as convergence criterion. By diagonalizing the hessian matrix, the stationary points of the potential energy hypersurface were characterized. Diagonal-

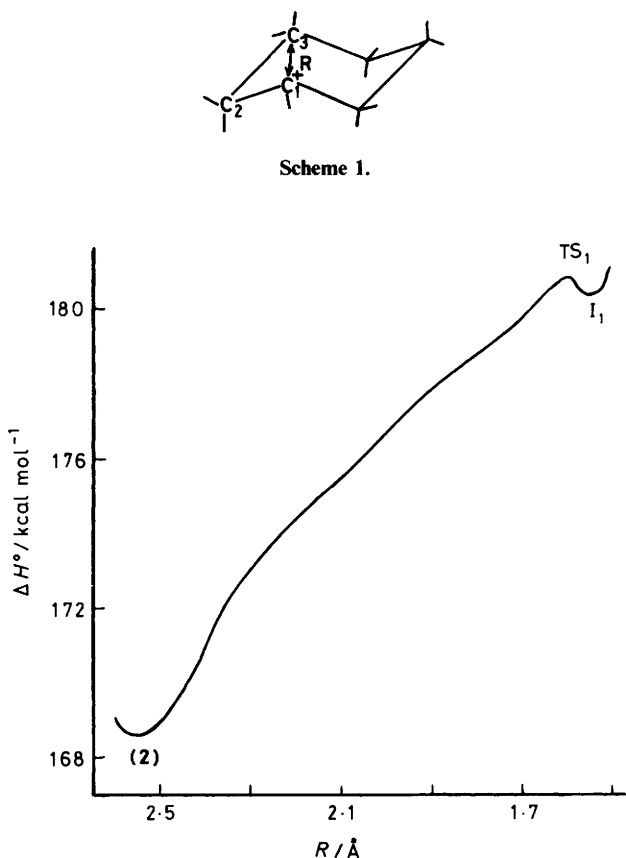


Figure 1. MINDO/3 energy profile corresponding to the formation of the bridged intermediate from cyclohexylium ion

ization was carried out using numerical derivatives (secant method) for interaction integrals and analytical computation for the density matrix (perturbation method).

Results and Discussion

First, the geometry of the cyclohexylium ion (2) was completely optimized, the heat of formation being 168.6 kcal mol⁻¹. This value agrees with that calculated by Harris.²⁵

To describe the initial events in the isomerization of the cyclohexylium ion to the 1-methylcyclopentylum ion, the distance *R* between the electronically deficient carbon atom C-1 and a carbon atom at the β-position, C-3, was chosen as the reaction co-ordinate (see Scheme 1). Figure 1 shows the variation of the heat of formation as a function of the distance *R*. All other structural parameters were optimized with respect to the total energy. A minimum appears at about 2.6 Å which corresponds to a cyclohexylium ion, and in the region 1.63–1.53 Å both a minimum *I*₁ and a maximum *TS*₁ appear. We cannot state that *I*₁ and *TS*₁ represent a true minimum or a true maximum (transition state), respectively, since we have imposed the constraint of a fixed value for *R*. To ensure that the selection of the reaction co-ordinate does not project the potential energy hypersurface improperly, the reaction path between the minima was followed in the inverse sense. No effects of chemical hysteresis were observed.

The geometry of the structure *I*₁ was completely optimized; all the eigenvalues of the hessian matrix were positive, hence this corresponds to a true minimum. The geometrical conformation of *I*₁ represents a structure where a hydrogen atom on C-3 has been partially transferred to C-2. This structure can be seen as a

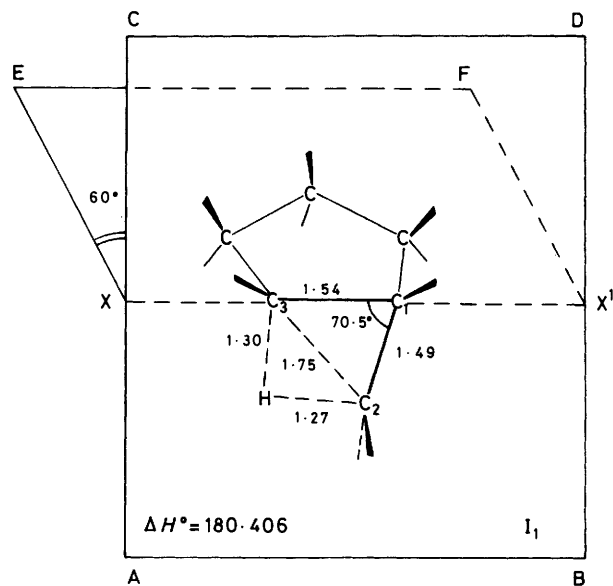


Figure 2. Geometrical conformation of the bridged intermediate *I*₁; heat of formation in kcal mol⁻¹ and distances in Å; three-membered ring in ABCD plane, five-membered ring in EFXX' plane

hydrogen-bridged conformation of a protonated cyclopropane ring type (see Figure 2).

To localize the transition state from the constrained maximum *TS*₁, the following steps²⁶ were carried out:

(1) Complete geometry optimization of the constrained maximum *TS*₁.

(2) Diagonalization of the hessian matrix corresponding to the final geometry obtained in (1). Only one negative eigenvalue appeared, close to zero, identifying this structure as a pseudo-transition state.

(3) Evaluation of the energy along the direction of the eigenvector associated with the negative eigenvalue in (2), since the displacement on the potential energy hypersurface in the region close to the true transition state must follow the eigenvector with negative eigenvalue.²⁷ Thus, we have constructed a displacement vector by multiplying this eigenvector by a scale factor λ .

(4) Search along λ until a maximum in energy is found (at λ_{\max}).

(5) Complete geometry optimization of the conformation corresponding to λ_{\max} .

(6) Diagonalization of the hessian matrix corresponding to the final geometry obtained in (5). At this stage the unique negative eigenvalue is clearly far from zero.

The evaluated energy of *TS*₁ is 12.1 and 0.3 kcal mol⁻¹ above the cyclohexylium ion and *I*₁, respectively (see Figure 3).

The C(1)C(2)C(3) angle, θ seemed to be the best reaction co-ordinate for controlling the process starting from *I*₁ and proceeding to the secondary 2-methylcyclopentylum ion. For increasing values of θ , the process reaches the products, but some discontinuities appear. However, for decreasing values of θ the process is directed towards the cyclohexylium ion, and large discontinuities break the energy profile. In all these cases, chemical hysteresis phenomena occur.

Therefore, one additional parameter was needed to describe the process. The distance *R* (as above) was chosen. Thus the minimum-energy reaction path on the bidimensional (*R* and θ) surface of the heat of formation was assigned as the reaction co-ordinate. This surface was calculated as a grid with a fixed step of 2° on the θ co-ordinate and an average step of 0.02 Å

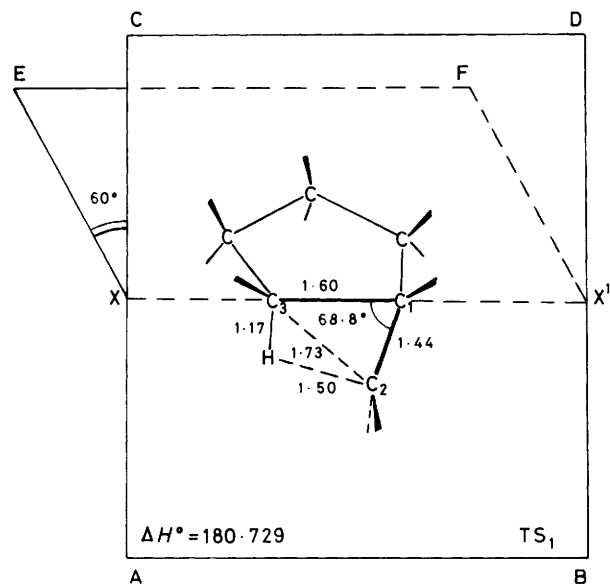


Figure 3. Geometrical conformation of the transition state TS_1 ; heat of formation in kcal mol⁻¹ and distances in Å; three-membered ring in ABCD plane, five-membered ring in EFXX' plane

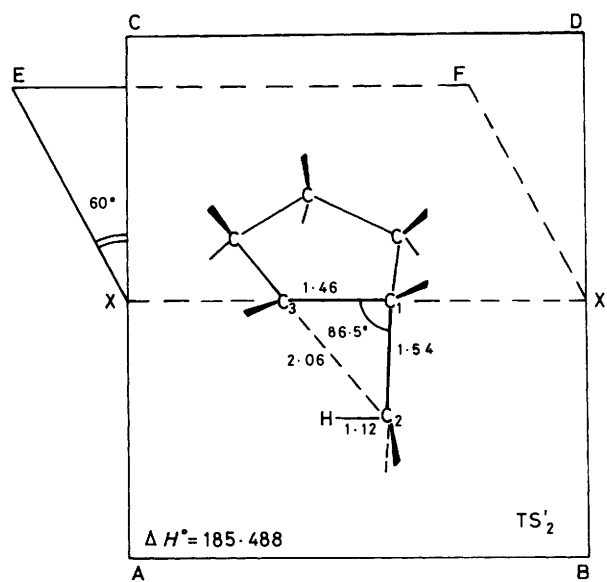


Figure 5. Geometrical conformation of the transition state TS_2' ; heat of formation in kcal mol⁻¹ and distances in Å; three-membered ring in ABCD plane, five-membered ring in EFXX' plane

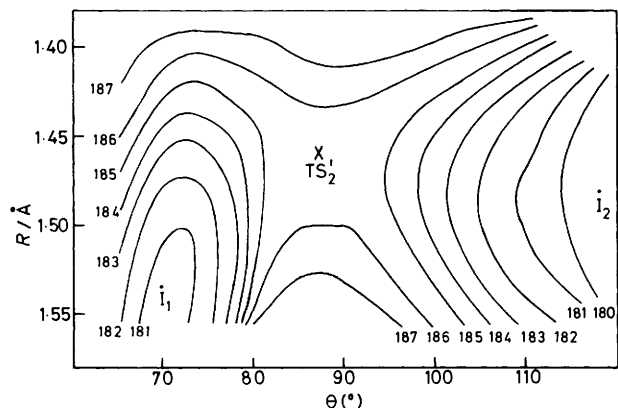


Figure 4. Projection of the MINDO/3 energy hypersurface for the β -cleavage of bridged intermediate I_1

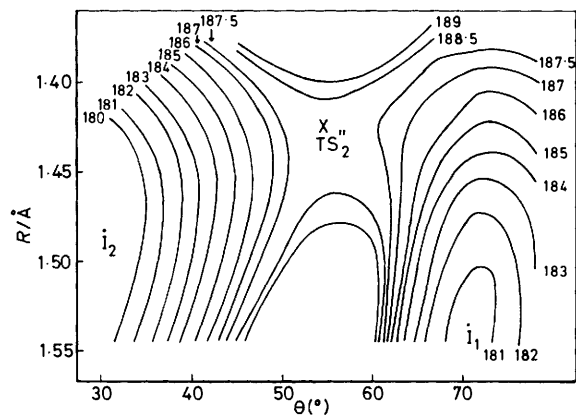


Figure 6. Projection of the MINDO/3 energy hypersurface for the α -cleavage of the bridged intermediate I_1

on the R co-ordinate. All the other geometrical parameters were optimized at each R, θ point. The calculations were carried out by fixing the R value and performing a scan on the θ values, starting from the I_1 geometry modified to have the required R and θ values, and then optimized. Afterwards the scan was followed in inverse sense, to avoid chemical hysteresis phenomena when necessary; in such cases graphical interpolation between the two scans provides the final value for each R, θ point.

Figure 4 shows the surface of heat of formation *versus* R and θ , starting from I_1 for increasing values of θ . Two valleys are present, corresponding to I_1 and the new intermediate I_2 (I_2 corresponds to a secondary 2-methylcyclopentylum ion), and an approach to a saddle point, TS_2' , is located at about R 1.46 Å, θ 86.0°. Complete optimization gives the true transition state TS_2' at R 1.464 Å, θ 86.5°, and diagonalization of the hessian matrix provides a unique negative eigenvalue. The structure of TS_2' shows that the bridging hydrogen atom in I_1 has been completely transferred to C-2 (see Figure 5). Furthermore, on the $TS_2' \rightarrow I_2$ path the methyl

group is partially twisted to reach the minimum conformation of I_2 . In an analogous fashion to the characterization of TS_2' , complete geometry optimization and further hessian diagonalization showed that I_2 is a true minimum. The TS_2' energy is 5.1 and 6.6 kcal mol⁻¹ above I_1 and I_2 , respectively.

An alternative way to describe the process $I_1 \rightarrow I_2$ is given by use of decreasing values of θ . Figure 6 shows the energy map built as described above. In this case an alternative transition state TS_2'' connects the I_1 and I_2 valleys. Choosing a geometry in the range R 1.43–1.44 Å, θ 55–57°, and optimizing this geometry completely, after diagonalization of the resulting hessian matrix, one obtains a peak, *i.e.* two negative eigenvalues, although one of them is very close to zero. Further efforts* to approach the true maximum (TS), which (following Murrell and Laidler²⁸) is close to any peak, were unsuccessful. We suggest that numerical problems arising from the non-quadratic nature of the hypersurface,²⁹ along with the presence of a large negative

* Such as calculations on a more narrow grid and diagonalization of the hessian matrix by either the secant or the perturbation method.

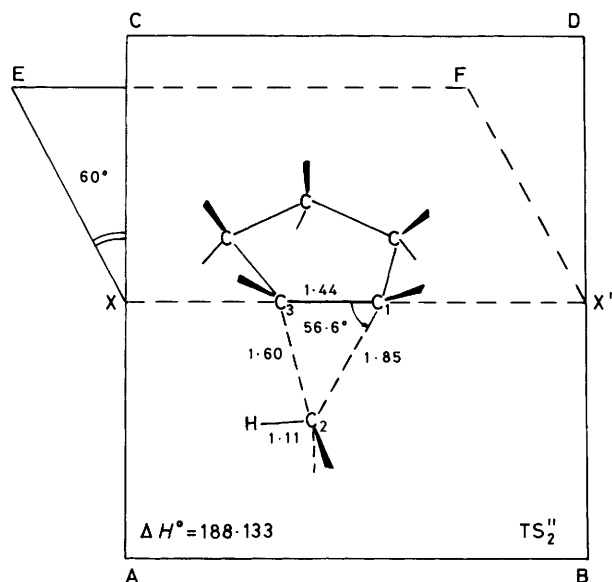


Figure 7. Geometrical conformation of the transition state TS_2'' ; heat of formation in kcal mol^{-1} and distances in Å; three-membered ring in ABCD plane, five-membered ring in EFXX' plane

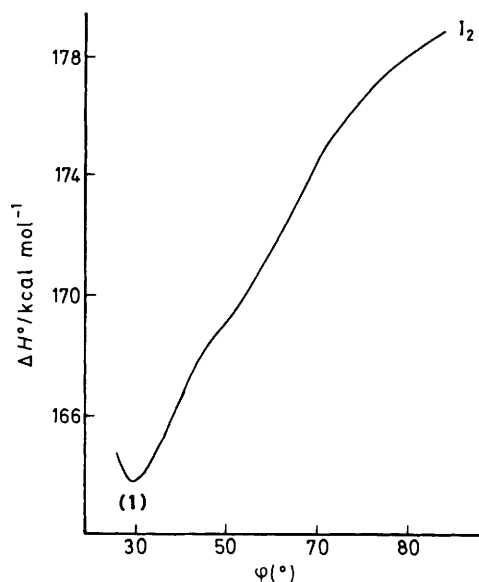
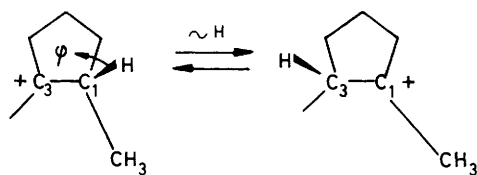


Figure 8. MINDO/3 energy profile corresponding to 1,2-hydrogen shift in I_2 to give 1-methylcyclopentylum ion



Scheme 2.

eigenvalue and one near-zero eigenvalue ('Don Quixote' saddle point²⁹) due to different curvatures along the maximum and minimum cross sections, are the justification for the anomalous behaviour of the surface in this region. The structure of this pseudo- TS_2'' resembles a distorted corner-protonated cyclopropane ring (see Figure 7). The energy is 7.6 and 9.2 kcal mol^{-1} above the I_1 and I_2 , respectively.

The intermediate I_2 transforms into a tertiary 1-methylcyclopentylum ion (1) via a 1,2-hydrogen shift between C-1 and C-3 (see Scheme 2). This process can be defined by the HC(1)C(3) angle, θ , and Figure 8 shows the energy profile versus θ . No discontinuities in energy and Wiberg indexes³⁰ are involved; hence it can be said that the 1,2-hydrogen shift occurs with no energy barrier, in agreement with MINDO/3 results.³¹

The tertiary carbenium ion was also optimized and the hessian matrix diagonalized to verify its minimum nature. The energy is 15.2 kcal mol^{-1} below I_2 . Figure 9 shows a scheme of the reaction profile in terms of the calculated heats of formation (see Table).

We have thus found a mechanistic model which describes the branching rearrangement of a cycloalkane in a simple fashion, since only a few parameters are needed to depict the reaction co-ordinate. The isomerization of cyclohexane is a very good model for testing the branching mechanism based on protonated cyclopropane-ring type intermediates, because of the rigidity of the five-membered ring involved, which eliminates most of the geometrical variables from the reaction co-ordinate, and simplifies the computational procedure without any loss of physically significant information.

The proposed overall mechanism, as shown in Figure 8,

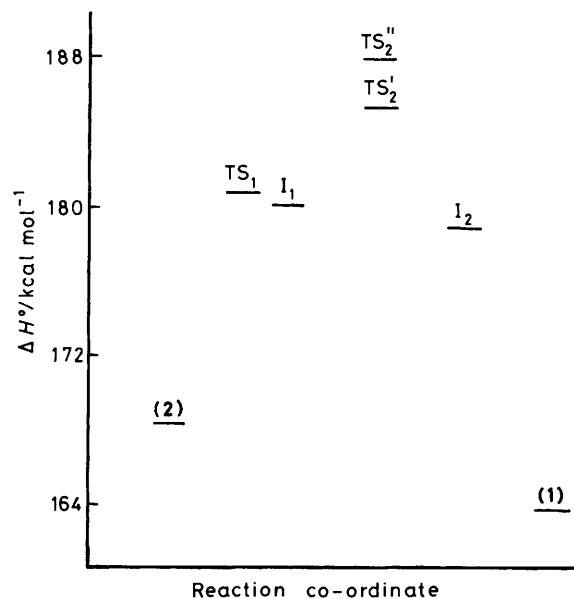
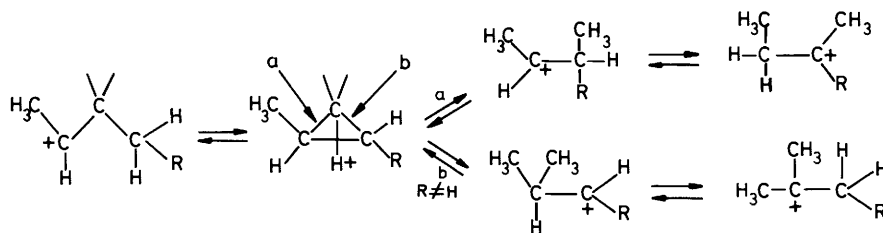


Figure 9. Relative energies of the reactants, intermediates, transition states, and products involved in cyclohexylum ion isomerization to 1-methylcyclopentylum ion

resembles closely the mechanism empirically suggested by Brouwer¹² for linear alkanes (see Scheme 3). Our intermediate I_1 can be related to Brouwer's intermediate of the protonated cyclopropane type. Both mechanisms allow two alternative routes starting from the intermediate of cyclopropane type, via α - or β -scission. Brouwer's mechanism for branching rearrangement of linear alkanes shows only the intermediates proposed. We have also calculated, characterized, and given the geometrical conformation of the transition states connecting them for the branching isomerization of cyclohexylum; the energy difference between TS_2' and the 1-methylcyclopentylum ion (1) (21.7 kcal mol^{-1}) can be related to the activation energy, and agrees well with the experimental value (17 kcal mol^{-1}).^{12b} The



Scheme 3.

Table. Standard heats of formation calculated by MINDO/3 (kcal mol⁻¹)

Species	ΔH°
(2)	168.609
I ₁	180.406
TS ₁	180.729
TS ₂ '	185.488
TS ₂ ''	188.133
I ₂	178.901
(1)	163.750

differences are ascribed to the known possible inaccuracies of the MINDO/3 method when one calculates the enthalpies of three-membered rings; hence we can conclude that the overall agreement is satisfactory.

The proposed model mechanism accounts for most of the experimental facts, such as activation energy, intermediates, and product structure; in view of its simplicity it may serve as a good general model for branching rearrangements of alkanes.

Acknowledgements

We thank the Centro de Cálculo de la Diputación Provincial de Valencia and Centro de Cálculo de la Universidad de Valencia for computing facilities.

References

- B. C. Gates, J. R. Katzer, and G. D. A. Schuit, in 'Chemistry of Catalytic Processes,' McGraw-Hill, New York, 1979, ch. 1.
- P. A. Jacobs, 'Carboniogenic Activity of Zeolites,' Elsevier, Amsterdam, 1977, ch. 4.
- J. W. Ward and R. C. Hansford, *J. Catal.*, 1969, **13**, 364.
- H. A. Benesi and B. H. C. Winquist, *Adv. Catal.*, 1978, **27**, 97.
- A. Corma and A. Lopez Agudo, *React. Kinet. Catal. Lett.*, 1981, **16**, 253.
- (a) Kh. Minachev, *Acta Phys. Chem.*, 1978, **24**, 5; (b) Kh. Minachev, V. I. Garanin, T. A. Isakova, V. V. Kharlamov, and V. I. Bogomolov, *Adv. Chem. Ser.*, 1971, **102**, 441.
- H. H. Voge, in 'Catalysis,' ed. P. H. Emmet, Reinhold, New York, 1958, vol. VI, ch. 5.
- H. S. Bloch, H. Pines, and L. Schmerling, *J. Am. Chem. Soc.*, 1946, **68**, 153.
- F. C. Whitmore, *J. Am. Chem. Soc.*, 1932, **54**, 3274.
- H. Hattori, O. Takahashi, M. Tagaki, and K. Tanabe, *J. Catal.*, 1981, **68**, 132; O. Takahashi and H. Hattori, *ibid.*, p. 144.
- G. A. Olah, *J. Am. Chem. Soc.*, 1972, **94**, 808; G. A. Olah, J. R. DeMember, and J. Shen, *ibid.*, 1973, **95**, 4952; G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 173.
- (a) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 210, 1435; (b) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 1971, **9**, 179; D. M. Brouwer, 'Reactions of Alkylcarbenium ions in Relation to Isomerization and Cracking of Hydrocarbons,' in 'Chemistry and Chemical Engineering of Catalytic Processes,' eds. R. Prins and G. C. A. Schuit, Sitthoff and Noordhoff, Alphen aan den Rijn, The Netherlands, 1980, p. 137.
- M. Saunders, P. Vogel, E. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, 1973, **6**, 53.
- G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Am. Chem. Soc.*, 1967, **89**, 2692.
- E. M. Arnett and C. J. Petro, *J. Am. Chem. Soc.*, 1978, **100**, 5408.
- M. Attina, F. Cacace, and P. Giacomello, *J. Am. Chem. Soc.*, 1981, **103**, 4711.
- R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285, 1294, 1302, 1307, 1311.
- M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1977, **99**, 377; M. J. S. Dewar and H. S. Rzepa, *ibid.*, p. 7432; C. W. Jefford, J. Mareda, J. C. Perlberg, and U. Burger, *ibid.*, 1979, **101**, 1370.
- M. J. S. Dewar, *Science*, 1975, **187**, 1037; *Chem. Br.*, 1975, **11**, 97.
- H. Lischka and H. J. Köhler, *Chem. Phys. Lett.*, 1978, **58**, 175; H. J. Köhler and H. Lischka, *J. Am. Chem. Soc.*, 1979, **101**, 3479.
- J. Planelles, J. Sanchez-Marín, F. Tomás, and A. Corma, *J. Chem. Soc., Perkin Trans. 2*, 1985, 333.
- P. Empedocles, *Theor. Chim. Acta*, 1969, **13**, 139; *Int. J. Quantum. Chem.*, 1969, **25**, 47.
- D. Rinaldi, *Comput. Chem.*, 1976, **1**, 109.
- D. Rinaldi, personal communication.
- J. M. Harris, S. G. Shafer, and S. D. Worley, *J. Comput. Chem.*, 1982, **3**, 208.
- J. Planelles, Thesis, University of Valencia, 1984.
- S. Glasstone, K. J. Laidler, and H. Eyring, in 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941.
- J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 371.
- P. G. Mezey, *Analysis of Conformational Energy Hyperfaces*, *Prog. Theor. Org. Chem.*, 1977, **2**, 127; *Chem. Phys. Lett.*, 1977, **47**, 70.
- K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.
- M. C. A. Donkersloot and H. M. Buck, *J. Am. Chem. Soc.*, 1981, **103**, 6549.

Received 11th March 1985; Paper 5/411