MINDO/3 Study of the Isomerization of 1-Methylcyclohexylium Ion to 1-Ethylcyclopentylium Ion. An Alternative Mechanism for this Branching Rearrangement

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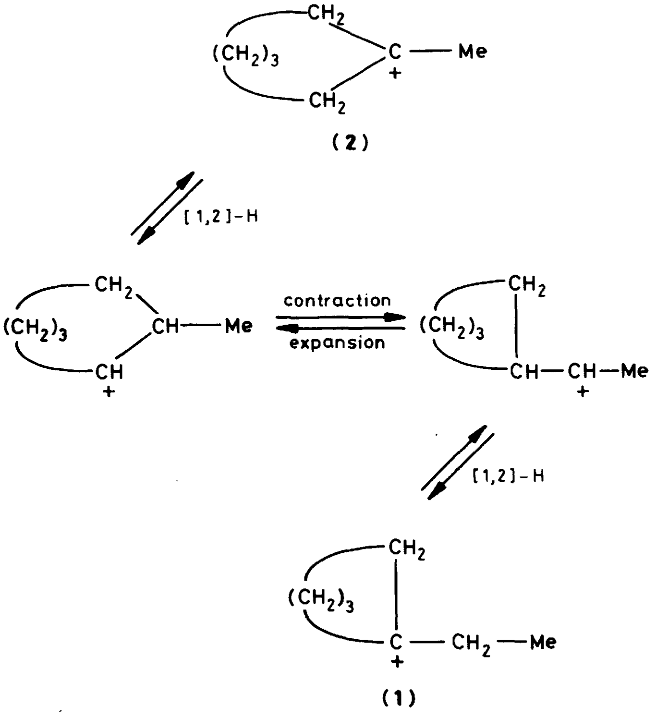
A MINDO/3 study of the rearrangement mechanism of 1-methylcyclohexylium ion to 1-ethylcyclopentylium ion is presented. The structures at three intermediates and three transition states have been calculated and characterized. The results show that a ring-contraction mechanism *via* a corner-protonated cyclopropane intermediate is a more adequate description of this process than one based on an H-bridged edge-protonated cyclopropane intermediate. The value calculated for the barrier height for the ring-expansion process (14.5 kcal mol^{-1}) is in good agreement with the experimental value (15.4 kcal mol^{-1}) for the activation energy. The proposed mechanism resembles the Wagner–Meerwein ring-contraction reaction.

Catalytic isomerization of alkanes in acidic media proceeds *via* carbocationic intermediates.[1–4] Reaction mechanisms based on carbenium ions† are assumed for heterogeneous reactions on solid acid catalysts,[1–4,6] as well as for homogeneous reactions in superacid media.[5,7,8] Alkane isomerization involves three steps: (*a*) formation of the carbeniums ion, (*b*) rearrangement of the carbenium ion intermediates, and (*c*) hydride ion abstraction to give the rearranged hydrocarbon. It is assumed that carbenium ion rearrangement is the slowest step, unless the initial hydrocarbon has no tertiary carbon atom.[8,9]

Carbenium ions give rise to two kinds of rearrangement,[8–10] branching and non-branching. The latter seems to take place *via* [1,2]-hydrogen and/or -alkyl shifts,[8–11] whereas for branching rearrangements it is assumed that the intermediate structure is of a protonated cyclopropane type,[8–10,12] since the [1,2]-alkyl- and/or -hydrogen-shift mechanism should lead to higher activation energies owing to the presence of primary carbenium ions.

A solid acid catalyst, such as H-Y zeolite, isomerizes methylcyclohexane to an equilibrium mixture of 1,2- and 1,3-dimethylcyclopentane and ethylcyclopentane[13] and from studies of the rearrangement of tertiary cycloalkyl carbocations Kirchen *et al.* have proposed a general ring-expansion or -contraction reaction. For medium-size rings (n = 5—7), the cyclohexyl ring is thermodynamically stable[14] and rearrangement of the tertiary 1-ethylcyclopentylium ion (**1**) to the tertiary 1-methylcyclohexylium ion (**2**) shows[14] a rate constant k of 1.4×10^{-3} s^{-1} at 214 K, and an activation free energy $\Delta G^{\neq}$ of 15.4 kcal mol^{-1}. A mechanism similar to the non-branching rearrangements (such as [1,2]-H,-R shifts) has been suggested[14] for the ring expansion–contraction rearrangement, where the second step involves the actual expansion or contraction (see Scheme 1).

In two previous papers[15,16] we have used the MINDO/3 method[17] to study the isomerization of the cyclohexylium to 1-methylcyclopentylium ion[15] and the tertiary 1-methylcyclohexylium to 1,2-dimethylcyclopentylium ion.[16] We proposed a rearrangement mechanism, involving an H-bridged edge-protonated cyclopropane intermediate, in accordance with the empirical mechanism proposed by Saunders[12] and Brouwer.[8–10] A mechanism involving a ring contraction starting from the initial cyclohexylium ion [Scheme 2(a)] has been discarded, since a primary carbocation, which would be much higher in energy, would have to be involved. However, the ring-contraction process starting from the secondary 2-methylcyclohexylium ion produces a secondary ethylcyclopentylium ion [Scheme 2(b)], and this seems to be an adequate alternative mechanism for simple ring contractions and expansions, in particular for the 1-methylcyclohexylium ⇄ 1-ethylcyclopentylium ion rearrangement.



Scheme 1. $\underset{(1)}{5^+ - \mathrm{Et}} \longrightarrow \underset{(2)}{6^+ - \mathrm{Me}}$; T 214K; $\Delta G^{\ddagger}$ 15.4 kcal mol^{-1}

We present here a MINDO/3 study of the rearrangement of the tertiary 1-methylcyclohexylium ion to the tertiary 1-ethylcyclopentylium ion. Our aim is to formulate a reaction mechanism for this rearrangement and to discuss the generality of the proposed mechanism[15,16] for branching rearrangements

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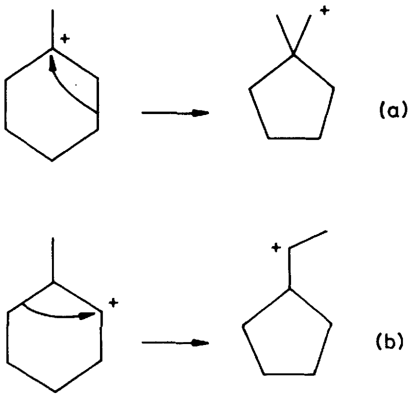
† Olah's nomenclature:[5] carbenium ions correspond to those in which there is a three-co-ordinated carbon atom, and carbonium ions to those which contain a pentaco-ordinated carbon atom.



Scheme 2.

of cyclohexyl and methylcyclohexyl carbocations, *via* an H-bridged edge-protonated cyclopropane intermediate, along with alternative mechanisms such as ring contractions–expansions which might be competitive.

Methods

All calculations were performed using the MINDO/3 method,[17] since the simple form of its Fock operator allows systematic investigations of the potential energy hypersurface, complete optimization of geometries, and characterization of the stationary points by diagonalization of the Hessian matrixes and analyses of their eigenvalues and eigenvectors. The MINDO/3 method is an appropriate tool to study chemical reactivity, provided that the energy values obtained by this method for transition states are of the same order of accuracy as those obtained for equilibrium states.[18] The results obtained for carbenium ions are comparable with *ab initio* results, and sometimes better, even when *ab initio* methods should include the calculations of the electronic correlation energy with moderately large basis sets.[19,20] In our experience, MINDO/3 adequately describes the mechanism of the branching rearrangement of medium-size cyclic carbenium ions.[15,16]

The minimum-energy reaction path (m.e.r.p.) for the 1-methylcyclohexylium $\rightleftharpoons$ 1-ethylcyclopentylium ion rearrangement has been calculated by means of the reaction co-ordinate method,[21] *e.g.* by choosing the geometrical parameters related to the reaction co-ordinate, and optimizing all the other variables at each point on the m.e.r.p. All the geometrical optimizations were performed with the metric variable procedure described by Rinaldi.[22] By diagonalizing the Hessian matrix, the stationary points of the potential energy hypersurface were characterized. All these calculations were carried out with GEOMO program.[23]

Results and Discussion

The crucial step in the isomerization mechanism of the 1-methylcyclohexylium to 1-ethylcyclopentylium ion is the ring-contraction step, connecting two secondary cations. Therefore, we have completely optimized the secondary 2-methylcyclohexylium ion. The resulting conformation, I'_1, shows a heat of formation of 169.3 kcal mol^{-1}, is a stationary point on the energy hypersurface, and has a classical structure.

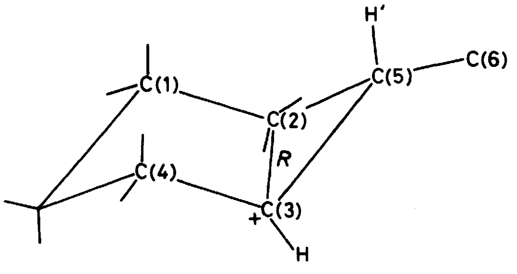


Figure 1.

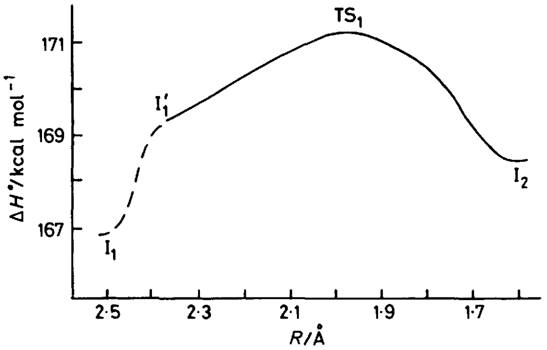
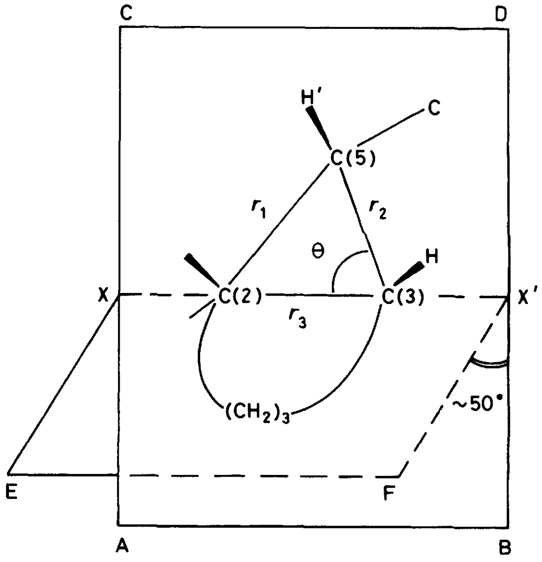


Figure 2. MINDO/3 Energy profile corresponding to the ring contraction of the secondary 2-methylcyclohexylium ion



System	r_1	r_2	r_3	θ(°)	Positive charge
I_2	1.90	1.43	1.61	76	C-5
TS_1	1.62	1.43	1.99	54	C-3
TS_2	2.00	1.44	1.60	83	C-5

Figure 3. Geometrical conformations of the intermediate I_2, and the transition states TS_1 and TS_2. The three-membered ring is in the ABCD plane. For I_2 and TS_2, the five-membered ring is nearly in the EFXX′ plane, and for TS_1 the five-membered ring is slightly puckered. Bond lengths are in Å

Figure 1 shows the geometrical parameter, R(C-3–C-2), chosen to describe the reaction co-ordinate starting from I'_1 and leading to the ring contraction. Figure 2 shows the variation of the heat of formation with the distance R. All the other geometrical parameters were optimized at each R value. Both a maximum and a minimum are present in the curve, at R *ca.* 2.0 and *ca.* 1.6 Å, respectively. The conformation corresponding to the restricted minimum was optimized completely, and the resulting conformation, I_2 (ΔH° 168.4 kcal mol^{-1}), was characterized as a true minimum (in which all the eigenvalues of the Hessian matrix were positive). The optimal geometry of I_2

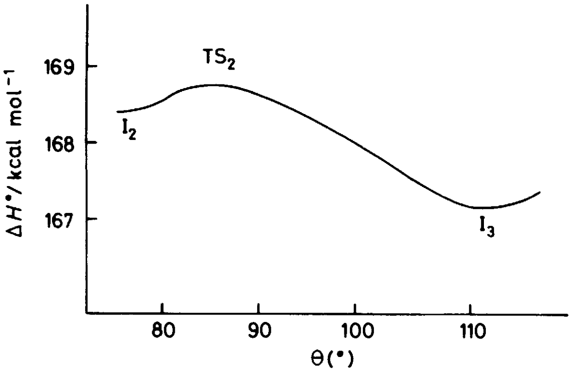


Figure 4. MINDO/3 Energy profile *versus* θ(C-5–C-3–C-2) for $I_2 \longrightarrow I_3$ path.

(Figure 3) shows a structure related to a corner-protonated cyclopropane intermediate in which a [1,2]-hydrogen shift does not occur between C-2 and C-5, unlike the intermediate obtained in the cyclohexylium[15] and 1-methylcyclohexylium[16] ion isomerization mechanisms. Also, the I_2 intermediate is more stable than the H-bridged edge-protonated cyclopropane intermediate (168.4 *versus ca.* 180 kcal mol^{-1}). The equatorial hydrogen atom on C–2 is not partially transferred to C–5 because at the presence of the C-5 methyl group, which stabilizes the positive charge.

From the restricted maximum on the plot of $\Delta H°$ *versus R*, the transition state TS_1 was obtained from the total optimization geometry. The stationary point, TS_1 ($\Delta H°$ 171.2 kcal mol^{-1}), was characterized as a true transition state (Figure 3) showing only a negative eigenvalue in its Hessian matrix. The distance *R* was used as the distinguishing co-ordinate and contained the main component of the associated eigenvector. If *R* is increased, starting from TS_1, a similar energy profile is obtained to that shown in Figure 2, until *R ca.* 2.40 Å is reached, and then a [1,2]-H′ shift occurs, to yield directly the tertiary 1-methylcyclohexylium ion (**2**). By characterizing the stationary point I'_1, as obtained above, a negative eigenvalue of its Hessian matrix is found, so it is not a true minimum on the energy hypersurface. The associated eigenvector shows its main components are the distance *R*, the H–C(3)–C(2) and H′–C(5)–C(3) bond angles, and the H–C(3)–C(2)–C(1) dihedral angle. By means of appropriate modification of these variables a stationary point I_1 is reached ($\Delta H°$ 166.7 kcal mol^{-1}), with the lowest eigenvalue being positive and close to zero.

To verify the minimum-energy path thus obtained, we have carried out the following test. Since the m.e.r.p. was calculated by optimizing the energy with respect to all geometrical parameters except *R*, it can be expected that the Hessian matrix restricted to the subspace of the optimized variables would have all-positive eigenvalues. Hence, we calculated and diagonalized the restricted Hessian matrix at several fixed values of *R*. This test is satisfied until *R* reaches 2.40 Å; for greater values of *R*, a negative eigenvalue is found, with an associated eigenvector whose components are the same as those mentioned above for the structure I'_1, with the exception of *R*. The dashed line in Figure 2 shows the projection of the energy *versus R*, obtained by following the search vector. As I_1 is reached (*R* 2.5 Å) the smallest eigenvalue of the Hessian matrix becomes increasingly close to zero.

Starting from the I_1 structure, a [1,2]-H′ shift yields the tertiary 1-methylcyclohexylium ion (**2**) ($\Delta H°$ 154.6 kcal mol^{-1}). The energy profile obtained for this shift, using the H′–C(5)–C(3) angle as the distinguishing co-ordinate, does not show an energy barrier, in accord with previous MINDO/3 results,[15] when the orbital orientation is favourable.

By means of the MOPAC program[24] we have confirmed the nature of the I_1 stationary point, minimizing the gradient norm[25] until an almost constant value is reached. Therefore, we can deduce from all these results that the energy hypersurface is very flat in the neighbourhood of I_1 and so this structure can be considered as a plateau rather than a local minimum, at least within the MINDO/3 framework.

The secondary ethylcyclopentylium ion I_3 can be reached from the intermediate I_2 through the m.e.r.p. calculated using the C(5)–C(3)–C(2) angle θ as the distinguishing co-ordinate. The energy profile obtained by increasing θ is rather flat (see Figure 4), showing only a small energy barrier. The corresponding transition state, TS_2, can be localized directly from the restricted maximum in Figure 4. The structure of the stationary point obtained ($\Delta H°$ 168.6 kcal mol^{-1}) is shown in Figure 3. The Hessian matrix shows a unique negative eigenvalue, and the associated eigenvector has the angle θ as its main component.

Optimization of the restricted minimum in Figure 4 gives the secondary ethylcyclopentylium ion, I_3, a true minimum ($\Delta H°$ 167.1 kcal mol^{-1}) in which all Hessian eigenvalues are positive. The tertiary 1-ethylcyclopentylium ion (**1**) is obtained from the second cation I_3 *via* a [1,2]-hydrogen shift (see Figure 5). If we choose as the distinguishing co-ordinate for this process either the distance *d*(H–C-5) or the angle θ H–C(5)–C(3), discontinuities in energy appear along with chemical hysteresis effects, mainly due to the orbital orientation of the intermediate I_3 which is not favourable. For a [1,2]-shift to have a low barrier, the empty *p* orbital on the cationic centre should have a dihedral angle equal to zero with the C–R bond, R being the migrating group.[26,27] The H–C(5)–C(3)–C(6) dihedral angle has a value of 6° for the I_3 secondary cation (see Figure 6). In order to describe this process adequately, an additional variable is needed to control the orbital orientation of the atoms bonded to C-5. The C(6)–C(5)–C(3)–C(2) dihedral angle (Φ) was chosen, and the two-dimensional energy surface obtained with the θ and Φ variables is shown in Figure 7. From the restricted maximum in this surface we obtained and characterized a true transition state TS_3 ($\Delta H°$ 168.7 kcal mol^{-1}), showing more favourable orbital orientation than the intermediate I_3 (see Figure 8).

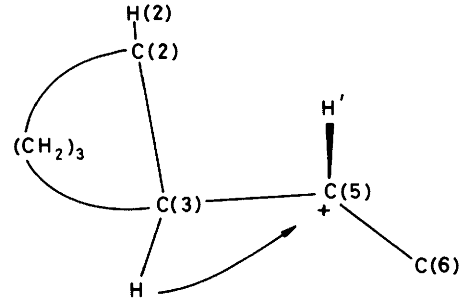


Figure 5.

The final point of this [1,2]-H shift is the tertiary 1-ethylcyclopentylium ion (**1**), a true minimum on the energy hypersurface ($\Delta H°$ 156.7 kcal mol^{-1}). This minimum, as it can be seen in Figure 7, lies on a long, flat, and narrow valley, in which several other minima are present, each corresponding to the different orientations of the ethyl group relative to the cyclopentyl ring. All the minima in this valley show similar energies and the connecting saddle points exceed them by only *ca.* 0.7 kcal mol^{-1}.

The values of the heat of formation of the transition states and intermediates as well as initial and final products are given in the Table.

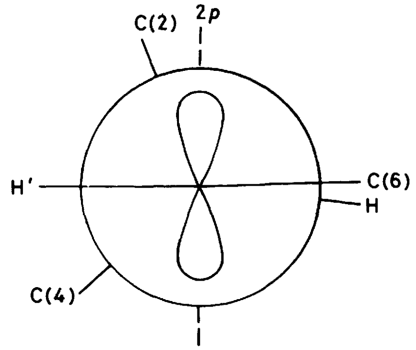


Figure 6. Newman projection along the C(5)–C(3) bond, showing the orbital orientation in the secondary ethylcyclopentylium ion I_3

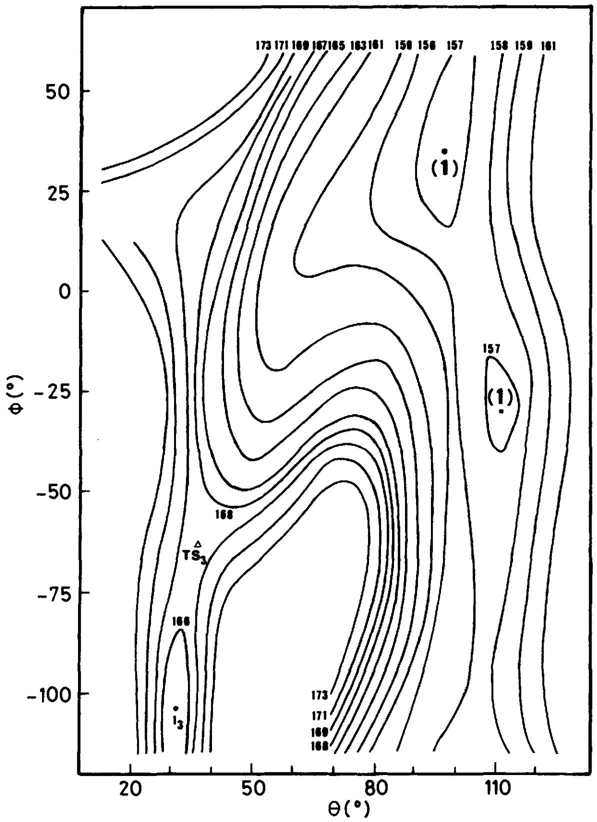


Figure 7. Two-dimensional projection of the MINDO/3 energy hypersurface *versus* θ(H–C-5–H-3), Φ(C-6–C-5–C-3–C-2) parameters for the $I_3 \longrightarrow$ (**1**) process. Heat of formation in kcal mol^{-1}

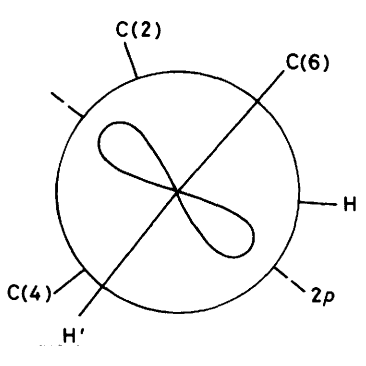


Figure 8. Newman projection along the C(5)–C(3) bond, showing the orbital orientation of the transition state TS_3

MINDO/3 Heats of formation (kcal mol^{-1}) of stationary points involved in the 1-methylcyclohexylium (**2**) $\rightleftarrows$ 1-ethylcyclopentylium (**1**) ion rearrangement

Species	$\Delta H°$
(**2**)	154.6
I_1	166.7
TS_1	171.2
I_2	168.4
TS_2	168.6
I_3	167.1
TS_3	168.7
(**1**)	156.7

The overall mechanism is similar to that proposed empirically by Kirchen *et al.*[14] for the ring contraction–expansion reactions of the tertiary cyclic carbocations. The main difference occurs in the presence of an intermediate I_2 in the contraction or expansion step. We have found the structure of this intermediate to be a corner-protonated cyclopropane, as opposed to the H-bridged edge-protonated cyclopropane found in the cyclohexylium and 1-methylcyclohexylium ion rearrangements,[15,16] where a similar corner-protonated cyclopropane would give an unstable primary carbocation. In the 2-methylcyclohexylium (I_1) $\rightleftarrows$ secondary ethylcyclopentylium (I_3) ring contraction, the methyl group stabilizes the charge localized on the α-carbon atom.

The difference in energy between (**1**) and TS_1, 14.5 kcal mol^{-1}, can be related to the overall activation energy in accord with the experimental value of 15.4 kcal mol^{-1} reported by Kirchen *et al.*[14] for the 1-ethylcyclopentylium (**1**) to 1-methylcyclohexylium (**2**) rearrangement. This agreement is not strange, since the MINDO/3 heats of formation for monosubstituted cycloalkyl carbocations show good accuracy.[28] MINDO/3 also reproduces well the energy difference between (**1**) and (**2**), *ca.* 2 kcal mol^{-1}, in agreement with the thermodynamic stability found for these cations.[14]

The results obtained suggest an alternative mechanism for this branching rearrangement to that proposed by Brouwer[8–10] and Saunders,[12] the main difference being the structure of the protonated cyclopropane intermediate involved in the ring contraction–expansion process. An alkyl group on the carbon atom α to an electron-deficient centre avoids the transfer of a hydrogen atom from the β carbon. The mechanism deduced can be related to the Wagner–Meerwein reaction.

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