Theoret. Chim. Acta (Berl.) 38, 241—244 (1975)

Relationes

INDO Calculations on the Sigmatropic [1, 5] H-Shift in 1,3-Cyclohexadiene and 1,3,5-Cycloheptatriene

A Homo-Cyclopentadienyl Transition State Model

Jan R. de Dobbelaere, Erica L. van Zeeventer, Jan W. de Haan, and Henk M. Buck
Dept. of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

Received October 24, 1974

INDO calculations have been performed for the activated complex of the [1, 5] H-shift in 1,3-cyclohexadiene and 1,3,5-cycloheptatriene. During the migration in the cyclohexadiene system a homoconjugation was calculated between the carbon atoms C_1 and C_5.

For cycloheptatriene it could be demonstrated that one double bond does not participate in the reaction.

Activation enthalpies are related to (homo)conjugation in the transition state of the reaction for cyclic conjugated dienes and trienes. The electron density on the migrating hydrogen can be related to the electron affinity of the ring system in the transition state.

Key words: Thermal sigmatropic hydrogen shifts – Homoconjugation – 1,3-cyclohexadiene and 1,3,5-cycloheptatriene, transition state geometry of ~

1. Introduction

Recently we reported a reaction pathway for the thermal sigmatropic [1, 5] H-shift in cyclopentadiene [1]. A detailed study of the geometry of the activated complex yielded a partial electron transfer from the migrating hydrogen to the nascent cyclopentadienyl system. This charge transfer was discussed in terms of "no-bond" and "dative" configurations. Very recently, extended calculations on this system appeared to be in good agreement with our results [2].

In this paper we extend our previously used model to cyclohexadiene and larger cyclic, conjugated dienes as well as trienes.

Table 1. Transition state geometries

Cyclohexadiene		Cycloheptatriene	
C_1–C_2 : 1.35 Å	$\alpha = 98°$	C_1–C_2 : 1.38 Å	$\alpha = 106°$
C_2–C_3 : 1.35	$\beta = 61°$	C_3–C_4 : 1.41	$\beta = 54°$
C_5–C_6 : 1.54	$\gamma = 22°$	C_4–C_5 : 1.47	$\gamma = 11°$
C_1–C_5 : 1.88		C_5–C_6 : 1.33	
C_2–C_4 : 2.27		C_1–C_3 : 2.33	
S –H'_5 : 0.93		C_4–C_7 : 2.31	
		S –H'_7 : 0.67	
$\varrho_{H'_5} = 0.95$		$\varrho_{H'_7} = 0.99$	

2. Results

The calculational procedures used in this study are very similar to those reported for cyclopentadiene [1]. In the symmetrical transition state of the [1, 5] H-shift we assume a three-center bond between the migrating hydrogen and two carbon atoms. The transition state geometries are given in Table 1 and Figs. 1 and 2. In Table 2 we compare the theoretical and the experimental activation enthalpies. The experimental value for cyclohexadiene, reported in this study, was obtained starting from 1,3-1D,4D-cyclohexadiene, using NMR-monitoring

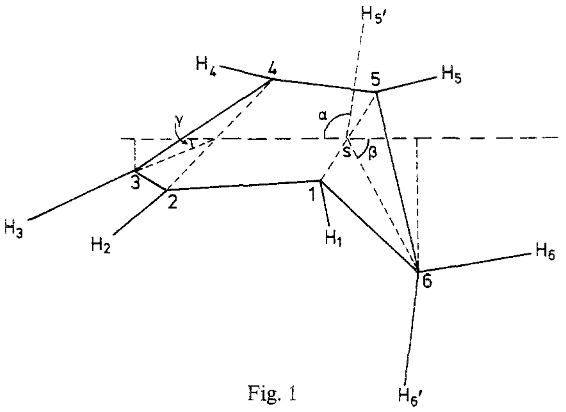

Fig. 1

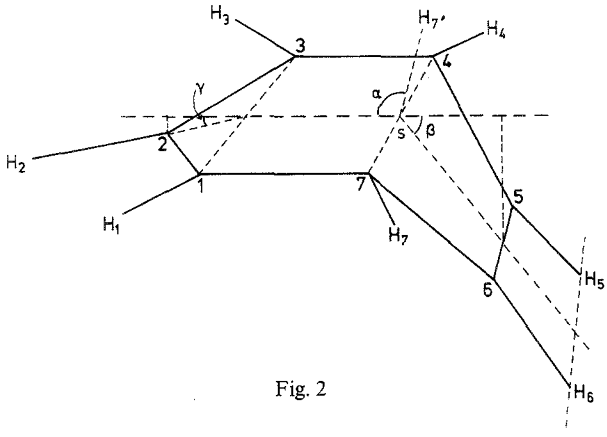

Fig. 2

Table 2. Activation enthalpies

	Ref.	$H^{\neq}_{\mathrm{exp}}$ (kcal/mole)	$H^{\neq}_{\mathrm{calc}}$ (kcal/mole)
Cyclopentadiene	[1, 3]	24	17
1,3-Cyclohexadiene		40	30
1,3-Cycloheptadiene	[4]	29	[a]
1,3-Cyclooctadiene	[5]	29	[a]
1,3,5-Cycloheptatriene	[6]	32	37
1,3,5-Cyclooctatriene	[7]	27	[a]

[a] See "Discussion".

of the reaction mixtures. Reaction temperatures ranged from 303° C to 330° C. More experimental details will be published elsewhere [11].

3. Discussion

In the previous study it was shown, how the stability of the cyclopentadienyl anion and -radical is reflected in the relatively low activation enthalpy for the [1, 5] H-shift in cyclopentadiene. Furthermore, it appeared that the charge transfer from the moving hydrogen to the cyclopentadiene system can be correlated with the electron affinity of the cyclic conjugated cyclopentadienyl system. Similar criteria will now be applied to larger conjugated ring systems.

The calculations for cyclohexadiene yield an electron density of 0.94 on the moving hydrogen (cf. 0.86 for cyclopentadiene). Obviously, in the cyclohexadienyl transition state the contribution of a homo-cyclopentadienyl radical, as well as the corresponding anion, is of great importance. This is illustrated by the relatively large overlap between the p_z-orbitals of C_1 and C_5. In the transition state proper the C_1–C_5 distance is 1.88 Å, versus 2.40 Å in the ground state. From ESR data it has been suggested already that the cyclohexadienyl system might be homoaromatic [8].

The electron affinity of a cyclopentadienyl system is larger than for a homocyclopentadienyl system which, in turn, is higher than for an open pentadienyl system. This explains the decreased contribution of the dative structure in the transition state of the cyclohexadiene system as compared with cyclopentadiene. In the cyclohexadiene system, the C_1–C_5 distance largely determines the energy of the transition state. In the transition state the C_1–C_6–C_5 angle is reduced to 75°, the C_1–C_5 distance is 1.88 Å (*vide supra*). Although in this study no rigorous calculations on 1,3-cycloheptadiene and 1,3-cyclooctadiene were performed, it is obvious that a homo-cyclopentadienyl contribution, similar to that in 1,3-cyclohexadiene, may be reached with considerably less strain imposed on the aliphatic part of the molecule. For the transition state of the 1,3-cycloheptadiene system a C_1–C_5 distance of ca. 1.9 Å is reached by changing the two aliphatic C–C–C angles from 109° to 95°.

The experimental activation enthalpies for [1,5] H-shifts in 1,3-cycloheptadiene and 1,3-cyclooctadiene are indeed lower than for 1,3-cyclohexadiene, see Table 2. At this point, it can be concluded that the picture, outlined in this and in the previous paper, explains the relative activation parameters involved in [1, 5] H-shifts in cyclic 1,3-dienes quite satisfactorily and in a mutually consistent manner.

In the transition state for cycloheptatriene, the migration origin and terminus are held apart by a non-flexible ethylenic bond, see Fig. 2. The calculated C_4–C_7 distance is 2.31 Å, leading to an almost completely open pentadienyl system instead of a homo-cyclopentadienyl system. The resulting lower electron affinity of the ring system (*vide supra*) is also reflected qualitatively in the fact that the migrating hydrogen carries a 0.99 electron density.

The remaining isolated double bond does not show any tendency towards conjugation, which, in itself, is in agreement with the Woodward-Hoffmann rules for sigmatropic reactions.

The calculated activation enthalpy for the H-shift in cycloheptatriene is 37 kcal/mole. This value is obtained by comparing the optimized transition state with the optimized ground state. However, a disturbing fact arises in complete optimization of the latter. This optimization leads to a norcaradiene system without the observation of an energy barrier on the reaction coordinate. So the calculated total energy of norcaradiene is lower than the total energy of cycloheptatriene. This is not in agreement with experimental facts concerning cycloheptatriene⇆norcaradiene equilibria [9]. This must be due to the known fact that INDO calculations underestimate the effect of ring strain. In order to avoid this unrealistic "optimization" of cycloheptatriene we fixed the distance C_1-C_6 at the experimental value of 2.51 Å [10] during the further optimization of the geometry. For this reason our calculated activation enthalpy has to be considered as a reasonable approximation only. The discrepancy between the calculated and experimental activation enthalpies in this case is to be ascribed mainly to an overestimation of the C_1-C_6 overlap in the ground state.

In 1,3,5-cyclooctatriene the experimentally observed activation enthalpy is lower than in cycloheptatriene, see Table 2. In the former system, migration origin and terminus are separated by a propene fragment compared with an ethene moiety in the latter system:

Scheme 1

Presumably, homocyclopentadienyl conjugation will be reached easier in the former than in the latter structure. If such a homoconjugation is achieved, the resulting electron affinity will exceed that of the "open" pentadienyl system in cycloheptatriene. In that case the resulting charge transfer from the moving hydrogen might be the origin of an extra stabilization by the interaction of the partially positive charged hydrogen with the isolated double bond in the system.

This anchimeric assistance of the "lone" double bond may contribute to the relatively low activation enthalpy for the H-shift in 1,3,5-cyclooctatriene.

References

1. de Dobbelaere, J. R., de Haan, J. W., Buck, H. M., Visser, G. J.: Theoret. Chim. Acta (Berl.) **31**, 95 (1973)
2. Shchembelov, G. A., Ustynyuk, Y. A.: J. Am. Chem. Soc. **96**, 4189 (1974)
3. Roth, W. R.: Tetrahedron Letters 1009 (1964)
4. Mironov, V. A., Chizkow, O. S., Kmielfeld, I. M., Akrem, A. A.: Tetrahedron Letters 499 (1969)
5. Glass, D. S., Boikess, R. S., Winstein, S.: Tetrahedron Letters 999 (1966)
6. ter Borg, A. P., Kloosterziel, H., van Meurs, N.: Rec. Trav. Chim. **82**, 717 (1963)
7. Glass, D. S., Zirner, J., Winstein, S.: Proc. Chem. Soc. **276** (1963)
8. Corvaja, C., Giacometti, G.: Theoret. Chim. Acta (Berl.) **14**, 352 (1969)
9. Ciganek, E.: J. Am. Chem. Soc. **93**, 2207 (1971)
10. Traetteberg, M.: J. Am. Chem. Soc. **86**, 4265 (1964)
11. Forthcoming Thesis of de Dobbelaere, J. R.

J. R. de Dobbelaere
Dept. of Organic Chemistry
Eindhoven University of Technology
P. O. Box 513
Eindhoven
The Netherlands