

Energy Calculation Involving Different steps of Dienone-Phenol Rearrangement so as to Predict the Most Facile Migratory Substituents From the Selected Species

Lijumon Lalremsanga

Champhai College, Champhai, Mizoram, India

Abstract:

The approach of this theoretical work is to study different steps involved in dienone-phenol rearrangement. Different substituents viz. Hydrogen, Methyl, Ethyl, Isopropyl and tertiary butyl groups were selected as the migratory substituents. Comparison was made between these substituents for their ability to accomplish 1,2 migration. Energy was determined for each substituents by using AM1, HF and B3LYP calculation. The molecular structure along with its substituent that corresponds to the minimum energy is considered as the most stable with easiest migration and the structure with its substituent giving the highest energy corresponds to the least probable migration. The energy of transition state with various substituents was taken as the major factor that determines the migration ability of substituent. The migratory aptitude of the migrating group is determined as the ability of the group to stabilize the carbo-cationic intermediate. The study includes plotting of the energy profile of the entire reaction from structure I to structure V.

Keywords: *Dienone-phenol rearrangement, migratory aptitude, 1,2 migration, AM1, HF and B3LYP calculation, carbo-cationic intermediate, energy profile.*

INTRODUCTION:

When 4,4-dialkyl cyclohexadienone is treated with acid, it is converted to phenol with migration of one of the two alkyl groups to the adjacent carbon. This is known as Dienone-phenol rearrangement. Dienone-phenol rearrangement is acid catalysed rearrangement and it involves isomerisation through carbo-cationic intermediates. An important step in the reactions is the 1,2- shift of a group within the intermediate cation. The driving force for the molecular rearrangement is the ability of gaining

aromaticity to form phenol from the non-aromatic dienone. At room temperature, when Dienones are treated with acetic anhydride solution in presence of a little sulphuric acid, protonation occurs at the carbonyl oxygen giving rise aryl carbo-cation stabilized by resonance. Creation of positive charge in the ring destabilizes the ring and the aryl carbo-cation undergoes rearrangement.

Rearrangement Via 1,2- shift in carbocationic system is an important phenomenon in some organic compound rearrangement. It has been studied

extensively for predicting the migration ability of substituent when there is a competition between dissimilar groups. The relative migratory aptitudes (RMA) describes which group will migrate in preference to another.

METHODOLOGY:

The semi empirical SCF – MO's method of the Gaussian 98 A . 11 . 2 package was used to calculate the gradient – corrected electron density functions, geometries, energies and frequencies of the dienone system. On the basis of this calculation, energy of different structures were determined. Firstly, hydrogen was taken as the migrating substituent and then methyl group, ethyl group, isopropyl group and tertiary butyl group. The structure of molecular species (or ionic species) with these various substituents involved in the reaction mechanism were calculated by using AM1, HF and B3LYP respectively. From the value of Energy calculated for different structures, the energy involved in the rearrangement reaction can be determined.

RESULT AND DISCUSSION:

The first step of the mechanism involves protonation at the oxygen of the carbonyl compound. The π -bond breaks up and form new σ -bond between oxygen and the incoming proton. This step results formation of positive center at the carbon adjacent to oxygen in the carbonyl. No change in hybridisation is

observed at the carbon but creation of positive charge destabilize the ring system and thus increase in energy is observed. Structure II is stabilised by two resonating structures where delocalization of π -electron distributes the positive center at C-1 and C-2. As the positive center is formed at the carbon adjacent to the migrating group, 1,2-shift of the migrating substituent takes place by passing a transition state. In the transition state bond angle and bond length changes cause the increase in energy in the whole system. The transition state gives rise to structure-V where complete transition of migrating group is observed. Deprotonation of structure-V results formation of new π -bond thus giving a more stable aromatic compound.

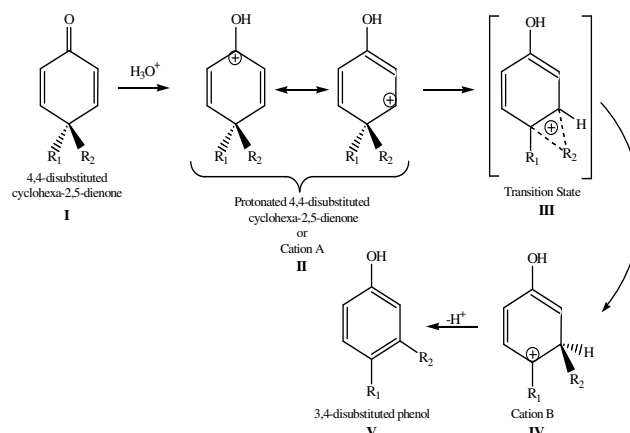


Figure-1: Different steps of dienone-phenol rearrangement where R_2 is the migratory substituent

Table-1: Energy calculated for successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R_2) in AM1 calculation (Kcal/mol)

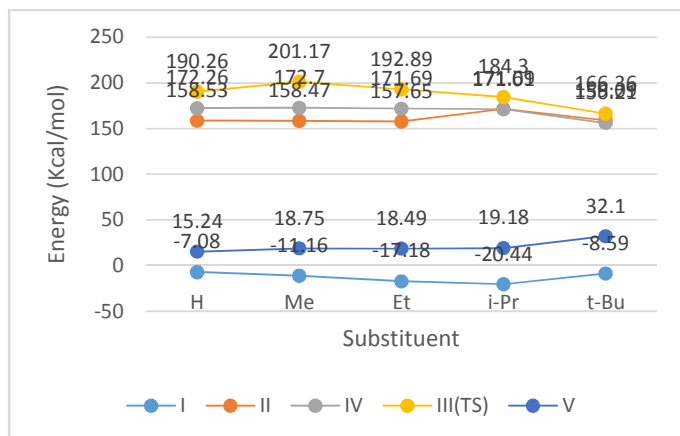


Figure-2: Graph showing energy of successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R₂) in AM1 calculation(Kcal/mol)

Table2: Energy calculated for successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R₂) in #HF/6-31G calculation

Structure	H	Me	Et	i-Pr	t-Bu
I	0	0	0	0	0
II	194.56	135.70	190.32	261.37	115.88
IV	201.67	202.93	204.12	267.45	140.59
III(TS)	222.68	223.94	225.00	288.53	202.05
V	10.16	11.91	12.73	76.76	12.04

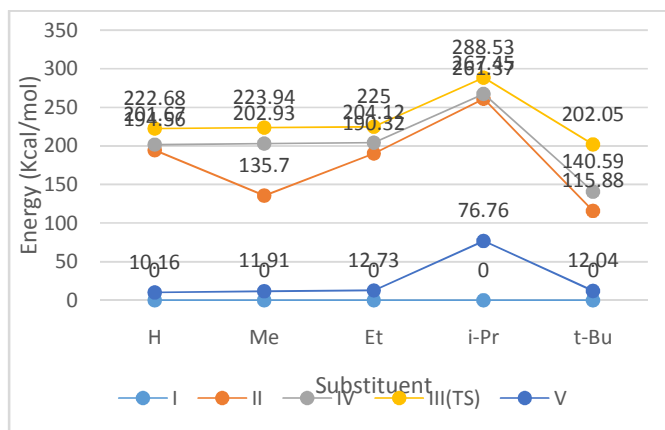


Figure-3: Graph showing energy of successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R₂) in #HF/6-31G calculation

Table3: Energy calculated for successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R₂) in #B3LYP/6-31G calculation (Kcal/mol)

Structure	H	Me	Et	Pr	Bu
I	0	0	0	0	0
II	197.22	166.08	199.42	206.63	193.27
IV	206.88	189.57	210.14	211.89	131.00
III(TS)	222.68	194.71	225.50	226.63	209.32
V	13.76	16.43	17.05	18.06	16.36

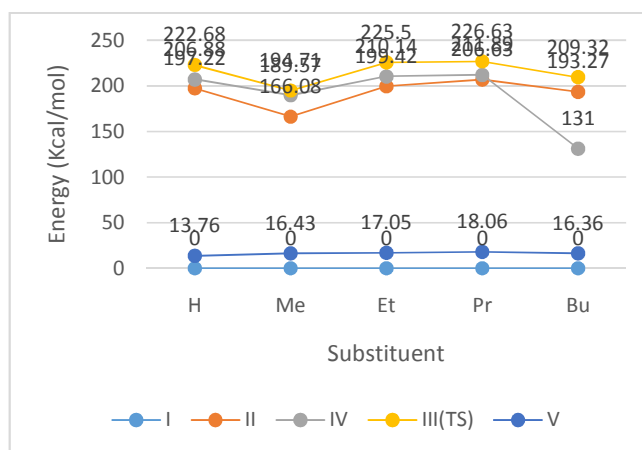


Figure-4: Graph showing energy of successive steps of the dienone-phenol rearrangement where; H, Me, Et, i-Pr, t-Bu are substituents (R₂) in #B3LYP/6-31G calculation

Structure	H	Me	Et	i-Pr	t-Bu
I	-7.08	-11.16	-17.18	-20.44	-8.59
II	158.53	158.47	157.65	171.69	159.09
IV	172.26	172.70	171.69	171.01	156.21
III(TS)	190.26	201.17	192.89	184.30	166.36
V	15.24	18.75	18.49	19.18	32.10

In all modes of calculations, the energy obtained for structure-I is exceptionally low, it is an indication of stability of structure-I compared to other structures. The high energy value in intermediate

cationic species may be attributed to the positive center created in the ring as a result of protonation. This positive charge destabilizes the ring structure by reason of increase in electronegativity at the positive center and a little bit angle strain in the system. Comparison of energy of transition states with various substituents shows that the transition structure with tertiary butyl group possess the lowest energy this is an indication of the stabilizing effect of tertiary butyl group to the positive center or geometry of the transition state.

CONCLUSION:

Calculated energy for different structures shows that protonation step in dienone-phenol rearrangement increases the energy and destabilizes the ring system by imparting positive charge to it but deprotonation stabilizes the molecular entity.

Although the order of energy in all calculations does not follow a regular pattern, the energy of transition state structure with tertiary butyl group occupy the lowest energy profile compared to transition state structure with other substituents. This implies that tertiary butyl stabilizes the transition state to a greatest extent in comparison to other groups. Therefore, migratory aptitude will be the highest among other substituents.

REFERENCES:

- [1] A. Sheldon *Fundamentals of Green Chemistry: Efficiency in Reaction Design*
- [2] Sad Moulay *The most well-known rearrangements in organic chemistry at hand. research and practice in europe 2002, vol. 3, no. 1, pp. 33-64*
- [3] Takuichi miki et al. *A phosphorylation of steroid and a Dienone-Phenol rearrangement leading to a secosteroidal aldehyde which has a strong toxicity*. Chemical and pharmaceutical bulletin
- [4] Draper RW. Et al. *An unusual dienone phenol rearrangement product formed during the synthesis of mometasone furoate*
- [5] James W. Pilkington and Anthony J. Waring. *Cyclohexadienone. Use of the dienone-phenol rearrangement in measuring migratory aptitudes alkyl groups*. Journal of American Society
- [6] Anthony J. Waring et al. *dienone-phenol rearrangement of bicyclic cyclohexa-2,5-dienones; Confirmation of a multistage mechanism*. Journal of American Society
- [7] Maria I.Colombo, Sebastiana A et al. *dienone-phenol rearrangement of santonin: A Comprehensive laboratory experiment for advanced undergraduate organic chemistry student*. The Chemical Educator December 2001, Volume 6
- [8] V.V Ershov, A.A Volod'kin and GN Bogdanov; *Phenol-Dienone rearrangement in the reaction of phenols*. Russian Chemical Reviews, Volume 32, Number 2
- [9] Yen-Long Vincent Hong B.S. *Migration Tendency substituent in some cationic rearrangement reaction*. A desertation in chemistry for doctor of phylosophy. Submitted to the graduate faculty of Texas Tech University. May, 1982
- [10] Saad Moulay. *The most well-known rearrangements in organic chemistry at hand*. Chemistry education: Research and practice in Europe. 2002, Vol 3, No 1, pp 33-64 (Review paper)
- [11] Christopher J Cramer(2004)*Essentials of computational Chemistry-Theories and Models*, 2nd Edn, John Wiley & Sons Ltd, 1-16.
- [12] Frisch M J et al, (2001) *GAUSSIAN 98, Revision A.11.2*, Gaussian, Pittsburgh, PA.
- [13] Steward J J P, (1990) *MOPAC MANUAL*, Sixth edition.
- [14] G.R. Chatwal-*Reaction mechanism and reagents in organic chemistry(2007)* Himalaya publishing house
- [15] S.M Mukherji and S.P Singh-*reaction mechanism in organic chemistry(1976)* Macmillan 16. Paula Yurkanis Bruice-*Organic chemistry Third edition(2006)* Pearson education
- [16] A.Sandoval, L. Miramontes, G.Rosenkranz and carl Djerrasi.*The dienone-phenol rearrangement* Journal of american chemical society, Vol 73, issues 3, pages 990-991 march 1951
- [17] Paul J Kropp- *On the mechanism of dienone-phenol rearrangement of A 2-Methyl-1,4-dien-3-one*. Tetrahedron Letters, Volume 3, issues 25, 1963, pages 1671-1676
- [18] Candelaria Goycoolea, Jose G. Santos and Jaime A. Valderrama-*Dienone-phenol rearrangement mechanism of 8,8-dimethyl and 6,8,8-trimethyl -naphthalene-1,4,5,(8H)- triones in acetic anhydride solution*. Journal of Chemical Society, Perkin Transaction2, issue 7, (1988)
- [19] Arnold R, Buckley J, Ritcher J. (1947).*The dienone - Phenol rearrangement* .Journal of American chemical society. 69 (10). 2322-2325.

- [20] Burnell R, Taylor W, (1954) Ring expansion. Part I. The Dienone – Phenol rearrangement of Spiro [5:5] undeca-1:4- Dinene-3-one. Journal of chemical Society (Resumed),3486-3488.