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Biswanath Dinda

Essentials of Pericyclic and Photochemical Reactions

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Biswanath Dinda

Essentials of Pericyclic and Photochemical Reactions

Springer

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Dedicated
to
my
parents and teachers

Preface

The part of pericyclic and photochemical reactions is the cornerstone of organic chemistry of the 20th century. Critical understanding of the principles of these reactions will be useful to design the synthesis of enormous organic compounds with high yields maintaining regio- and stereoselectivity. In this book, utilizing my long teaching experience, I have aimed to present the basic principles of pericyclic and photochemical reactions in the student's comprehension by citing numerous examples with references to develop a thorough and sound sense of actuality on the subject. Literature citations throughout the text will be helpful to the students and teachers, who want to get the access to the original work of the factual material. This book is not designed to be comprehensive with respect to the experimental details and evidences on which the reaction mechanisms are based. The main objectives of this book are to develop a broad understanding and scientific thinking of the students on the subject. The book will help teachers to motivate students in their scientific imagination on the subject for new application in industrial fields avoiding hazardous chemicals. A large number of excellent and representative problems at the end of each chapter and their answers in Appendix-1 of the book will help the students for their self-evaluation on the lessons of the chapter.

This book is basically designed for the students of postgraduate and M. Phil levels. However, the students of upper undergraduate levels in chemistry may use it for advancement of their knowledge on the subject. The book will also be useful for students to compete for different qualifying examinations after postgraduation.

I have consulted three excellent books, Advanced Organic Chemistry by F. A. Carey and R. T. Sundberg, Pericyclic Reactions by I. Fleming and Principles and Applications of Photochemistry by B. Wardle at several points in writing this book.

I wish to acknowledge the technical assistance of my students, Dr. Saikat Das Sarma, Dr. Rajarsi Banik, Dr. Indrajit Sil Sarma, Dr. Prasenjit Rudrapaul, Smt. Ankita Chakraborty, Sri Sukhen Bhowmik, Sk. Nayim Sepay, Sri Subhadip Roy, Sri Arnab Bhattacharya and my son, Dr. Subhajit Dinda for typing of the major part of the manuscript.

I would appreciate to receive the letters from teachers and students on errors, questions, criticisms and suggestions on this book so that I may improve this book in the forthcoming edition.

Finally, I like to acknowledge to my wife, Chitralekha, and our children, Subhajit and Manikarna, and son-in-law Shekhar for their constant encouragement and patient endurance. I am grateful to my publishers for their support and interest in this endeavour.

Agartala, Tripura, India
January 2016

Biswanath Dinda

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Abbreviations

acac	Acetylacetonate
BINAP	Bis-(2,2'-diphenylphosphinyl)-1,1'-binaphthalene
BINOL	Binaphthol
Boc	*Tertiary*-butoxycarbonyl [Me_3COCO]
BOX	Bisoxazoline
Bz	Benzyl [$PhCH_2$]
DBMP	6-di-*tert*-butyl-4-methyl phenol
DBP	Dibutyl phthalate
DBU	Diazabicycloundecane
DMA	Dimethylallene
DPM	Di-π-methane
ee	Enantiomeric excess
Et	Ethyl [C_2H_5]
FVP	Flash vacuum pyrolysis
HMPA	Hexamethylphosphoramide
HOMO	Highest occupied molecular orbital
hv	Ultraviolet or visible irradiation
IL	Ionic liquid
i-Pr	Iso-propyl[Me_2CH]
KHMDS	Potassium hexamethyldisilazane or potassium bis(trimethylsilyl) amide [$(Me_3Si)_2NK$]
LDA	Lithium diisopropylamide [$LiNi\text{-}Pr_2$]
LUMO	Lowest unoccupied molecular orbital
Me	Methyl [CH_3]
MTAD	N-methylthiazolinedione
N,N-DEA	N, N-diethanolamine [$NH(CH_2CH_2OH)_2$]
n-Pr	Normal-propyl [$MeCH_2CH_2$]
ODPM	Oxa-di-π-methane
PET	Photo-induced electron transfer
Ph	Phenyl [C_6H_5]

PhH	Benzene
P_i	Phosphate, inorganic
Py	Pyridine
rt	Room temperature
sens	Sensitizer
SOMO	Singly occupied molecular orbital
TADDOL	α,α,α,α-tetraaryl-1,3-dioxolane-4,5-dimethanol
TBDPS	*Tert*-butyldiphenylsilyl
TBS	*Tert*-butylmethyl silyl
t-Bu	Tertiary-butyl [Me_3C]
TCB	Tetracyanobenzene
THF	Tetrahydrofuran
TMS	Trimethylsilyl[Me_3Si]
Ts	Tosyl [4-MeC_6H_4]
TS	Transition structure

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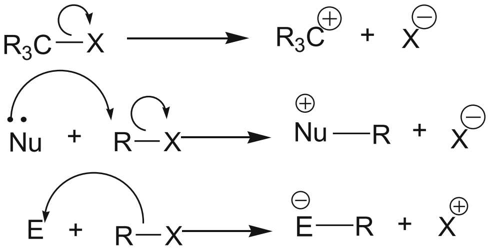
Part I
Pericyclic Reactions

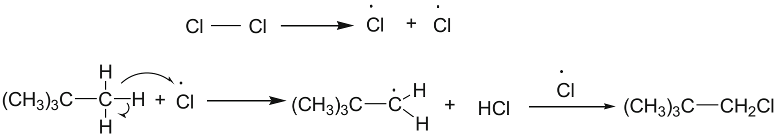
Chapter 1
General Aspects of Pericyclic Reactions

1.1 Introduction

Reactions in Organic Chemistry are broadly classified into three major categories—ionic, radical, and pericyclic. Ionic reactions involve the formation of ionic intermediates by movement of pair of electrons in one direction of a covalent bond. In a unimolecular reaction, it occurs by ionization process and in a bimolecular reaction, it occurs when one component acts as a nucleophile (or electron pair donor) and another component as electrophile (or electron pair acceptor). For example,



Radical reaction involves the homolytic cleavage of a covalent bond by movement of single electrons in opposite directions. The movement of a single electron is represented by fish hook arrow. For example,



2,2-dimethyl propane

1-chloro-2,2-dimethyl propane

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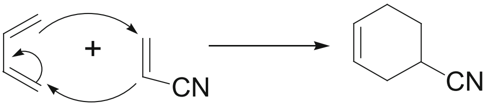
Pericyclic reactions involve the continuous flow of electrons in cyclic transition states (TS) by breaking and making of bonds in a concerted process, without formation of an intermediate. Hence, these reactions are known as concerted reactions [1]. These reactions are insensitive to solvent polarity and free radical initiators or inhibitors. These reactions are activated by heat (thermal) or light (photochemical). Detailed study of the mechanisms of these reactions by Woodward and Hoffmann [2] predicted that these reactions occur by the maintenance of symmetry properties of the orbitals of reactant(s) and product(s). The Diels–Alder reaction is a typical example.



A Diels-Alder reaction

1.2 Molecular Orbitals and Their Symmetry Properties

In pericyclic reactions, the reactivity of the reactions can be explained on the basis of Perturbational Molecular Orbital (PMO) theory [3]. The basic postulate of PMO theory is that a chemical reaction takes place by the perturbation of molecular orbitals (MOs) of reactants on heating and on irradiation with light. The degree of perturbation is a function of degree of overlapping interactions of the atomic orbitals in an MO. These interactions are strongest among the orbitals close in energies. These orbital overlapping interactions produce degenerate MOs of different energies. The suitable degenerate MOs take part in the reactions to give products through cyclic TSs in a concerted process. The interactions of two atomic orbitals will produce two MOs, one of them will be stabilized and other will move to higher energy. The linear combination of atomic orbitals is known as LCAO theory or PMO theory. The shapes of the MOs that are formed by the linear combination of atomic orbitals (LCAO) are related to the shapes of atomic orbitals. The MOs are denoted by ψ (psi) and atomic orbitals by Φ (phi). Dewar and Hoffmann first developed a general PMO method to explain the reactivity in organic chemistry. To illustrate the idea, let us consider a diatomic molecule where an MO formed by the combination of atomic orbitals of A and B is represented as

$$\psi = \Phi_A + \Phi_B$$

Quantum mechanics shows that the linear combination of two wave functions gives two combinations and hence two MOs are generated from two-component atomic orbitals. One MO is bonding orbital, more stable than the component atomic orbitals and other one is an antibonding orbital, less stable than the component orbitals.

$$\psi_+ = \Phi_A + \Phi_B \text{ (bonding MO)}$$
$$\psi_- = \Phi_A - \Phi_B \text{ (antibonding MO)}$$

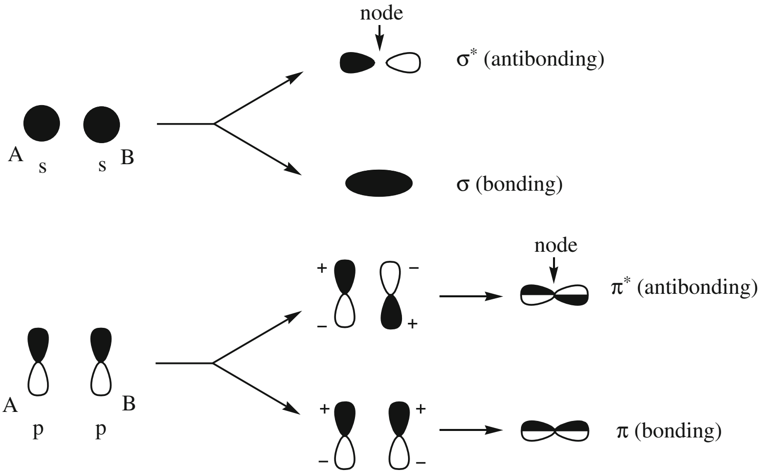
The MOs that have resulted from overlap of various kinds of atomic orbitals are shown in Fig. 1.1.

Similarly, the linear combination of three p-orbitals in allyl system will give rise to three new MOs ψ_1, ψ_2 and ψ_3. The antibonding interactions increase the energy of the MO. Thus, the energy of ψ_2 is higher than that of ψ_1 and ψ_3 is of higher energy than ψ_2. The wave functions and their symmetry in relation to the mirror plane are shown in Fig. 1.2.

Similarly, the linear combination of four atomic π orbitals in 1, 3-butadiene will generate four MOs ψ_1, ψ_2, ψ_3, and ψ_4 (Fig. 1.3).

Next, the linear combination of six atomic p-orbitals of 1,3,5-hexatriene will give rise to six MOs. The wave functions and symmetry properties of these MOs are shown in Fig. 1.4.

On the basis of the above examples of polyene systems, the symmetry properties of MO, ψ_n of a linear conjugated polyene are summarized in Table 1.1.



Presented + and - are mathematical signs

Fig. 1.1 Formation of bonding and antibonding orbitals

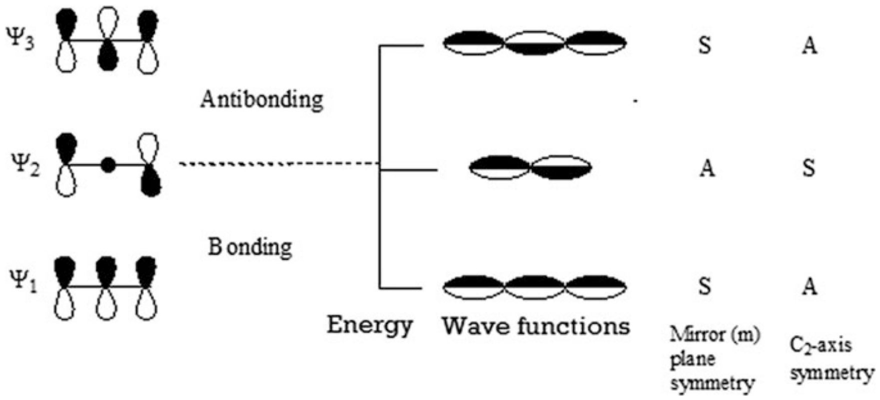


Fig. 1.2 Molecular orbitals formation in allyl systems

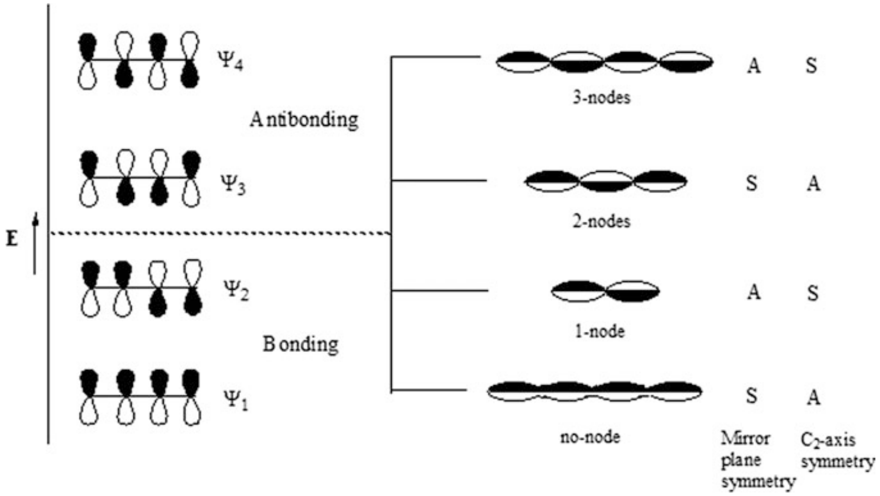


Fig. 1.3 Molecular orbitals of 1,3-butadiene and their symmetry properties. (S means symmetric and A means antisymmetric)

1.3 Classification of Pericyclic Reactions

Pericyclic reactions are classified into four classes. These are electrocyclic reactions, cycloadditions, sigmatropic rearrangements, and group transfer reactions.

Electrocyclic reactions are characterized by the creation of a ring from an open-chain conjugated system with the formation of a new σ bond at the ends of the conjugated system or its reverse process.

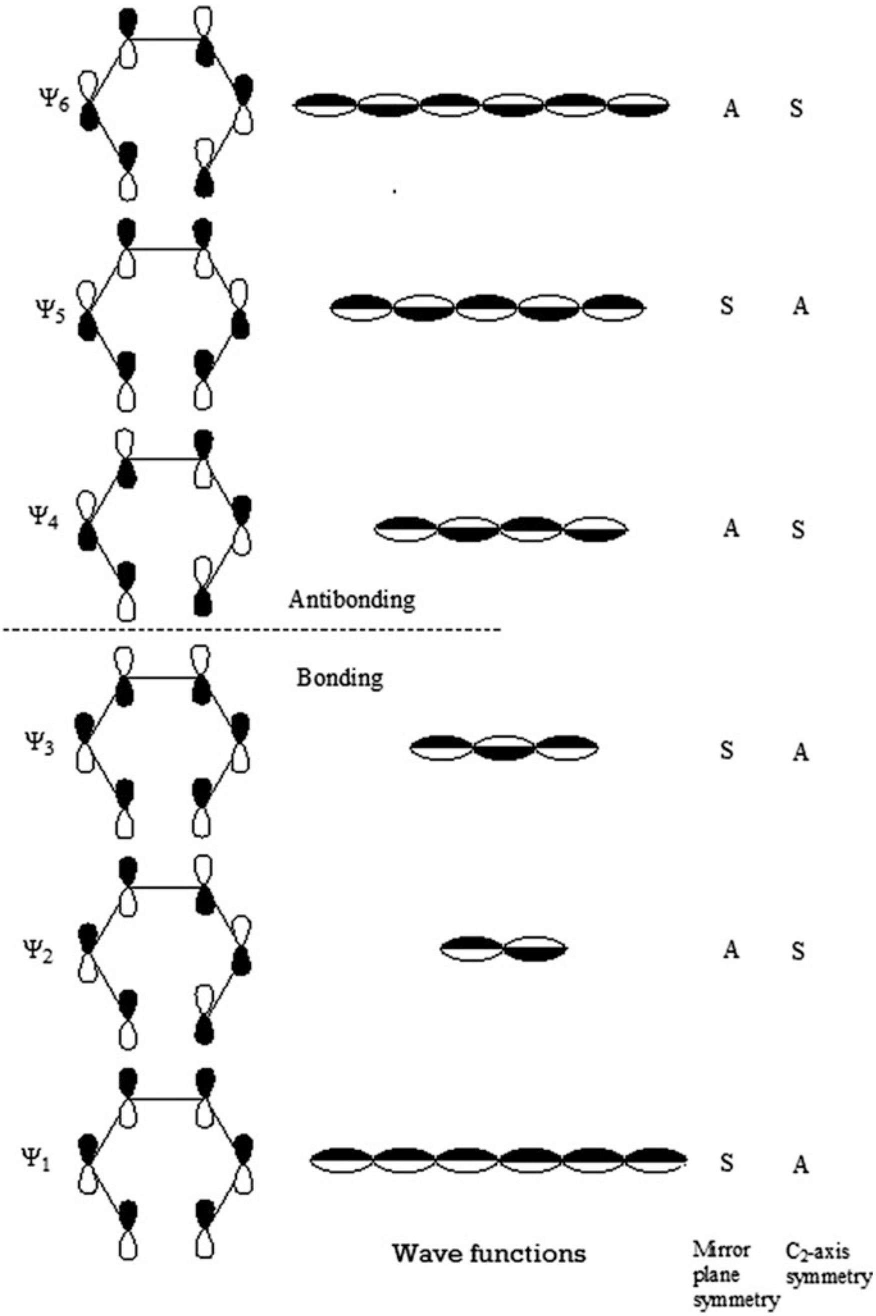
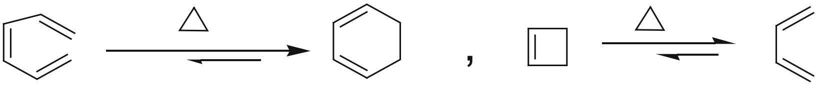


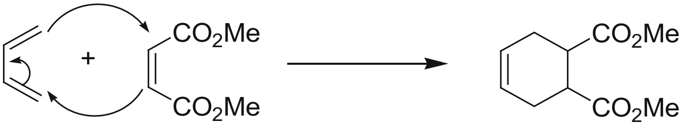
Fig. 1.4 Molecular orbitals of 1,3,5-hexatriene and their wave functions and symmetry properties

Table 1.1 Symmetry properties of the orbital ψ_n of a linear conjugated polyene

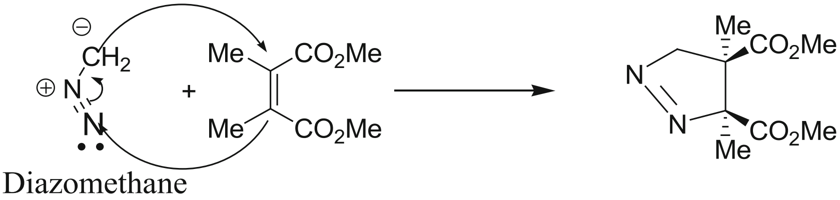
Wave function	Nodes	m-symmetry	C2-symmetry
ψ_{odd}: ψ_1, ψ_3, ψ_5	0 or even	S	A
ψ_{even}: ψ_2, ψ_4, ψ_6	odd	A	S



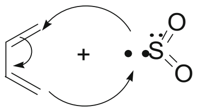
Cycloaddition reactions are characterized by the addition of two π-systems by the formation of two new σ bonds, at the ends of both components, with the reduction of one π-bond from each component, e.g., Diels–Alder reactions.



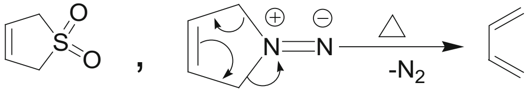
1, 3-Dipolar cycloadditions are another family member of cycloaddition reactions, e.g.,



Cheletropic reactions are a special group of cycloadditions or cycloreversions in which two σ bonds are made or broken from the same atom.



Cheletropic addition



Cheletropic extrusion

Sigmatropic rearrangements are characterized by the movement of a σ bond to a more distant terminus of an adjacent π system followed by movement of the π system to accommodate this new σ bond, e.g.,