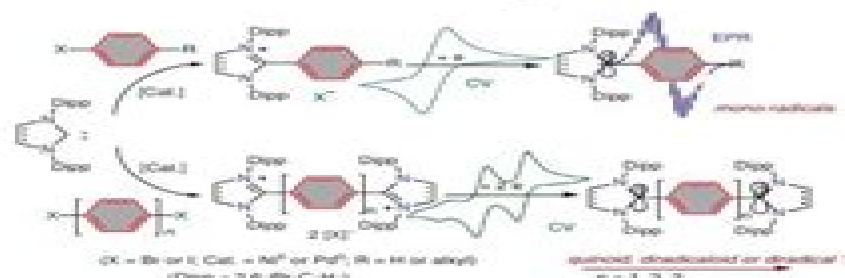


Stable Carbon-Centered Radicals Based on N-Heterocyclic Carbenes

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Abstract Carbon-centered radicals and diradicaloids based on classical N-heterocyclic carbene (NHC) scaffolds are readily accessible in crystalline solids. The presence of an aryl (Ar) substituent at the C2-position is the key to the remarkable stability of these open-shell species as it provides appropriate room for the spin-density delocalization. Two catalytic as well as high-yielding protocols have been developed to install a suitable aryl group at the C2-position of NHCs. The spin-density in mono-radicals (NHC[•])⁺ is mostly located on the parent carbene-carbon (C2) atom. The bridging of two NHCs through a phenylene spacer (C₆H₄), enables the isolation of various p-quinodimethane (p-QDM) derivatives, which may be considered as open-shell Kekulé diradicaloids. The diradical character of these NHC-analogues of Thiels (n = 1), Chichibabin (n = 2), and Müller (n = 3) hydrocarbons [(NHC)(C₆H₄)_n(NHC)] can be tuned by a rational choice of the size and/or the topology of spacers. In this account, the synthesis, structure, and properties of this new class of radical hydrocarbons is presented.

- 1 Introduction
- 2 NHC-Monomericals
- 3 NHC-Diradicaloids
- 4 Conclusion

Key words: radical, diradical, diradicaloid, carbene, hydrocarbon, heterocycle, open-shell, paramagnetic

1 Introduction

Radicals are fundamental intermediates¹ and they play crucial roles in numerous biological² and industrially important processes.³ In general, radicals are short-lived species and, therefore, in a condensed phase, spontaneously react with surrounding (solvent, precursor, or by-product) molecules, undergo self-decomposition or dimerization to eventually form closed-shell products.⁴ Consequently, syn-

thetic access to thermally stable⁵ radicals for detailed structural investigations has been a subject of intense fundamental interest for augmenting our understanding about chemical bonding and electronic structure.⁶ In addition, stable radicals are also highly promising class of compounds for their potential applications in materials science and emerging areas.⁷ This is because of their unique optical, electronic, and magnetic properties.^{8a,b} The potential of stable radicals as unique building blocks for the design of next-generation advanced functional materials for applications in optoelectronics, spintronics, and solar cells is substantial.⁹ The incorporation of stable radicals into artificial molecular machines (AMMs) is very appealing because an electron's spin can be much easier and more precisely controlled, even with a smaller energy input, than a charge.¹⁰ In this context, carbon-centered radicals have special advantages because of their planar trivalent nature, which promises structural diversity and elaborate designs. Stable radicals are also of immense interest as active materials in organic radical batteries (ORBs).¹⁰ These so-called 'eco batteries' have the potential to be cheaper, safer, and longer-lasting than current metal-based batteries and, thus, are of ever-growing importance in our modern technology-based society.¹¹ This becomes evidently more appealing if such radicals are derived from 1,3-imidazoli(n)ium precursors, which are promising electrolytes for battery applications. In recent years, radical catalysis has also emerged as an important tool in organic synthesis.¹²

Stable Radicals and Radicaloids

In 1900, Gomberg isolated the first stable radical, the triphenylmethyl I (Scheme 1).¹³ This seminal report marked the dawn of stable radical chemistry. I, however, undergoes self-association in the condensed phase, yielding the α -dimer II. Although the delocalization of the unpaired electron

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S-Centered Radicals Zeev B. Alfassi, 1999-03-22 S centered Radicals Edited by Ben Gurion University of the Negev Israel Sulfur containing radicals formed from sulfur emissions from natural sources e.g. volcanoes power plants and from car exhausts play an important role in our atmosphere In the living cell sulfur constitutes an essential part of the defence against oxidative damage and in the course of this mechanism is transformed into a variety of sulfur free radical species S centered Radicals deals with the organic radicals containing sulfur atoms RS RSO RSO₂ and R₃S and the inorganic radicals SH and SO_x This is the book to bring together all the recent developments of S centered radical chemistry This area is extremely important to organic synthetic chemists and environmentalists S centered radicals are of increasing interest in biochemistry and medicine due to S containing amino acids and S S bonds in proteins Sulfur radicals are also involved in polymer chemistry and photonic materials as well as in radiation protection and nutrition This title is the essential volume for anyone working in sulfur chemistry

Carbon-Centered Free Radicals and Radical Cations Malcolm D. Forbes, 2010-01-22 Covers the most advanced computational and experimental methods for studying carbon centered radical intermediates With its focus on the chemistry of carbon centered radicals and radical cations this book helps readers fully exploit the synthetic utility of these intermediates in order to prepare fine chemicals and pharmaceutical products Moreover it helps readers better understand their role in complex atmospheric reactions and biological systems Thoroughly up to date the book highlights the most advanced computational and experimental methods available for studying and using these critically important intermediates Carbon Centered Free Radicals and Radical Cations begins with a short history of the field of free radical chemistry and then covers A discussion of the relevant theory Mechanistic chemistry with an emphasis on synthetic utility Molecular structure and mechanism focusing on computational methods Spectroscopic investigations of radical structure and kinetics including demonstrations of spin chemistry techniques such as CIDNP and magnetic field effects Free radical chemistry in macromolecules Each chapter written by one or more leading experts explains difficult concepts clearly and concisely with references to facilitate further investigation of individual topics The authors were selected in order to provide insight into a broad range of topics including small molecule synthesis polymer degradation computational chemistry as well as highly detailed experimental work in the solid liquid and gaseous states This volume is essential for students or researchers interested in building their understanding of the role of carbon centered radical intermediates in complex systems and how they may be used to develop a broad range of useful products

Electron Spin Resonance Spectroscopy of Organic Radicals Fabian Gerson, Walter Huber, 2006-03-06 Electron spin resonance spectroscopy is the method used to determine the structure and life expectancy of a number of radicals Written by Fabian Gerson and Walter Huber top experts in the field of electron spin resonance spectroscopy this book offers a compact yet readily comprehensible introduction to the modern world of ESR Thanks to its comprehensive coverage ranging from fundamental theory right up to

the treatment of all important classes of organic radicals and triplet state molecules that can be analyzed using ESR spectroscopy this unique book is suitable for users in both research and industry Instead of using complex mathematical derivations the authors present a readily understandable approach to the field by interpreting sample spectra and classifying experimental data In short the ideal book for newcomers to the subject and an absolute must have for everyone confronted with ESR spectroscopy and wanting to become acquainted with this widely used method of analysis

CRC Handbook of Organic Photochemistry and Photobiology, Third Edition - Two Volume Set Axel Griesbeck, Michael Oelgemöller, Francesco Ghetti, 2019-04-05 The only combined organic photochemistry and photobiology handbook As spectroscopic synthetic and biological tools become more and more sophisticated photochemistry and photobiology are merging making interdisciplinary research essential Following in the footsteps of its bestselling predecessors the CRC Handbook of Organic Photochemistry and Photochemistry

Free-Radical-Induced DNA Damage and Its Repair Clemens Sonntag, 2006-03-20 The free radical chemistry of DNA had been discussed in some detail in 1987 in my book The Chemical Basis of Radiation Biology Obviously the more recent developments and the concomitant higher level of understanding of mechanistic details are missing Moreover in the living cell free radical DNA damage is not only induced by ionizing radiation but free radical induced DNA damage is a much more general phenomenon It was therefore felt that it is now timely to review our present knowledge of free radical induced DNA damage induced by all conceivable free radical generating sources Originally it had been thought to include also a very important aspect the repair of DNA damage by the cell's various repair enzymes Kevin Prise Cancer Campaign Gray Laboratory London was so kind to agree to write this part However an adequate description of this strongly expanding area would have exceeded the allocated space by much and this section had to be omitted The directors of the Max Planck Institut für Strahlenchemie now MPI für Bioanorganische Chemie Karl Wieghardt and Wolfgang Lubitz kindly allowed me to continue to use its facilities after my retirement in 2001 Notably our librarian Mrs Jutta Theurich and her right hand help Mrs Rosemarie Schreier were most helpful in getting hold of the literature I thank them very much Without their constant help this would have been very difficult indeed

Handbook of Bond Dissociation Energies in Organic Compounds Yu-Ran Luo, 2002-12-26 So many compounds so many experiments reported by so many researchers using so many methods Finding reliable data on bond dissociation energies BDEs can be like looking for a needle in a haystack But these data are crucial to work in chemical kinetics free radical chemistry organic thermochemistry and physical organic chemistry so where does one turn With data on almost 2900 bonds in 2500 organic compounds the Handbook of Bond Dissociation Energies in Organic Compounds is the first comprehensive collection of experimental BDE data Author Dr Yu Ran Luo has spent more than 10 years collecting assessing and tabulating BDE experiment results and presents them here in a well organized easy to use series of tables For each compound the tables list up to five recent experimental values indicate which is the recommended value give the method used to determine each value and provide

references for each value An outstanding format and complete indexing both by compound name and by compound class make searching for data quick and easy While experimental BDE values carry inherent uncertainties the value of this compilation does not There is simply no other resource that provides as much data With this book when you need data on a particular bond dissociation energy you ll find it within just a few minutes

Membrane Lipidomics for Personalized Health Carla Ferreri, Chrysostomos Chatgililoglu, 2015-08-31 Lipidomics is an important aspect of personalized medicine in relation to nutrition and metabolism This approach has become important due to the substantial presence of nutraceuticals in the market since it gives personalized criteria on how to choose the right nutraceutical strategy for both prevention and for quality of life This multi disciplinary textbook uses a simple and practical approach to provide a comprehensive overview of lipidomics and their connection with health and nutrition The text is divided into two parts Part 1 outlines the basics of lipidomics and focuses on the biochemical and nutritional aspects with descriptions of the analytical methods employed for the examination of cell membrane fatty acid composition Part 2 familiarizes the reader with the use of membrane lipidomic diagnostics in practical health care using health conditions as examples to introduce the concept of lipidomic profiles in different physiological and pathological situations including prevention Through the various properties of membrane lipidomics readers will be able to combine the molecular status of the cell membrane with the evaluation of the subject for personalized nutritional and nutraceutical strategies **Membrane Lipidomics for Personalized Health** will be beneficial to biologists biochemists and medical researchers as well as health care professionals pharmacists and nutritionists seeking in depth information on the topic

Introduction to Dynamic Spin Chemistry Hisaharu Hayashi, 2004 Readership Graduate students researchers and industrialists in chemistry physics and biology

Free Radicals and Oxidation Phenomena in Biological Systems Roberfroid, 1994-12-14 This work offers an analysis of the biological processes mediated by free radicals from a toxicological point of view providing easy access to information in an integrated coherent presentation The chemistry and biochemistry of all principal types of radical are explained and the multiple forms in which radicals participate in living organisms are investigated This work should be of use to biochemists pharmacologists pharmaceutical researchers food scientists and technologists nutritionists toxicologists chemists biologists and graduate students in these disciplines

Reactive Species Detection in Biology Frederick A. Villamena, 2016-10-23 *Reactive Species Detection in Biology* From Fluorescence to Electron Paramagnetic Resonance Spectroscopy discusses the reactive oxygen species that have been implicated in the pathogenesis of various diseases presenting theories chemistries methodologies and various applications for the detection of reactive species in biological systems both in vitro and in vivo Techniques covered include fluorescence high performance chromatography mass spectrometry immunochemistry and electron paramagnetic resonance spectroscopy Probe design and development are also reviewed in order to advance new approaches in radical detection through synthesis computations or experimental applications Reviews all current advances in radical detection Emphasizes chemical structures

and reaction schemes fundamental to radical detection and identification Describes the uses advantages and disadvantages of various probe designs Examines new approaches to radical probe development **Oxidation of Amino Acids, Peptides, and Proteins** Virender K. Sharma, Steven E. Rokita, 2012-11-06 Explains the role of reactive intermediates in biological systems as well as in environmental remediation With its clear and systematic approach this book examined the broad range of reactive intermediate that can be generated in biological environments detailing the fundamental properties of each reactive intermediate Readers gain a contemporary understanding of how these intermediates react with different compounds with an emphasis on amino acids peptides and proteins The author not only sets forth the basic chemistry and nature of reactive intermediates he also demonstrates how the properties of the intermediates presented in the book compare with each other Oxidation of Amino Acids Peptides and Proteins begins with a discussion of radical and non radical reactive species as well as an exploration of the significance of reactive species in the atmosphere disinfection processes and environmental remediation Next the book covers such topics as Thermodynamics of amino acids and reactive species and the effect of metal ligand binding in oxidation chemistry Kinetics and mechanisms of reactive halogen oxygen nitrogen carbon sulfur and phosphate species as well as reactive high valent Cr Mn and Fe species Reactivity of the species with molecules of biological and environmental importance Generation of reactive species in the laboratory for kinetics studies Oxidation of amino acids peptides and proteins by permanganate ferryl and ferrate species Application of reactive species in purifying water and treating wastewater With this book as their guide readers will be able to assess the overall effects of reactive intermediates in biological environments Moreover they ll learn how to apply this knowledge for successful water purification and wastewater treatment **Recent Trends In Radiation Chemistry** James F Wishart, B S Madhava Rao, 2010-02-09

Recent Trends in Radiation Chemistry is a state of the art review of the present status and future trends in the field of radiation chemistry research It covers a broad spectrum of topics ranging from the historical perspective instrumentation of accelerators in the nanosecond to femtosecond region through the use of radiation chemical methods in the study of antioxidants and nanomaterials radiation induced DNA damage by ionizing radiation involving both direct and indirect effects to ultrafast events in free electron transfer radiation induced processes at solid liquid interfaces and the recent work on infrared spectroscopy and radiation chemistry The contributors to the book are world renowned specialists The book is unique in that it covers a wide spectrum of topics that will be of great interest to beginners as well as experts Recent data on ultrafast phenomena from the recently established world class laser driven accelerators facilities in the US France and Japan are reviewed There has not been a significant book covering the important field of radiation chemistry for the last 5 years This timely book which includes highlights of recent work will appeal not only to the specialists working in the area but also to other researchers involved in related specialties remove a remove **Radiation Chemistry** C.D. Jonah, B.S.M. Rao, 2001-08-23 During the twentieth century radiation chemistry emerged as a multi faceted field encompassing all areas of

science Radiation chemical techniques are becoming increasingly popular and are being routinely used not only by chemists but also by biologists polymer scientists etc Radiation Chemistry Present Status and Future Trends presents an overall view of the different aspects of the subject The chapters review the current status of the field and present the future opportunities in utilizing radiation chemical techniques This will be of interest to chemists in general and in particular to radiation chemists chemical kineticists photochemists physical organic chemists and spectroscopists In view of the diverse nature of the field the book is a multi authored effort by several experts in their particular areas of research Six main areas both basic and applied were identified and the book is organized around them The topics were selected in terms of their relative importance and the contribution of radiation chemistry to the general areas of chemistry biology and physics The topics covered are as diverse as gas phase radiation chemistry the use of radiation chemical techniques the treatment of water pollutants the chemical basis of radiation biology and muonium chemistry The book also contains an update of the next generation electron accelerators

Encyclopedia of Physical Organic Chemistry, 6 Volume Set Zerong Wang, Uta Wille, Eusebio Juaristi, 2017-04-17 Winner of 2018 PROSE Award for MULTIVOLUME REFERENCE SCIENCE This encyclopedia offers a comprehensive and easy reference to physical organic chemistry POC methodology and techniques It puts POC a classical and fundamental discipline of chemistry into the context of modern and dynamic fields like biochemical processes materials science and molecular electronics Covers basic terms and theories into organic reactions and mechanisms molecular designs and syntheses tools and experimental techniques and applications and future directions Includes coverage of green chemistry and polymerization reactions Reviews different strategies for molecular design and synthesis of functional molecules Discusses computational methods software packages and more than 34 kinds of spectroscopies and techniques for studying structures and mechanisms Explores applications in areas from biology to materials science The Encyclopedia of Physical Organic Chemistry has won the 2018 PROSE Award for MULTIVOLUME REFERENCE SCIENCE The PROSE Awards recognize the best books journals and digital content produced by professional and scholarly publishers Submissions are reviewed by a panel of 18 judges that includes editors academics publishers and research librarians who evaluate each work for its contribution to professional and scholarly publishing You can find out more at proseawards.com Also available as an online edition for your library for more details visit Wiley Online Library

Comprehensive Toxicology, 2017-12-01 Comprehensive Toxicology Third Edition Fifteen Volume Set discusses chemical effects on biological systems with a focus on understanding the mechanisms by which chemicals induce adverse health effects Organized by organ system this comprehensive reference work addresses the toxicological effects of chemicals on the immune system the hematopoietic system cardiovascular system respiratory system hepatic toxicology renal toxicology gastrointestinal toxicology reproductive and endocrine toxicology neuro and behavioral toxicology developmental toxicology and carcinogenesis also including critical sections that cover the general principles of toxicology cellular and

molecular toxicology biotransformation and toxicology testing and evaluation Each section is examined in state of the art chapters written by domain experts providing key information to support the investigations of researchers across the medical veterinary food environment and chemical research industries and national and international regulatory agencies Thoroughly revised and expanded to 15 volumes that include the latest advances in research and uniquely organized by organ system for ease of reference and diagnosis this new edition is an essential reference for researchers of toxicology Organized to cover both the fundamental principles of toxicology and unique aspects of major organ systems Thoroughly revised to include the latest advances in the toxicological effects of chemicals on the immune system Features additional coverage throughout and a new volume on toxicology of the hematopoietic system Presents in depth comprehensive coverage from an international author base of domain experts

Molecular Basis of Oxidative Stress Frederick A. Villamena, Henry Jay Forman, 2025-02-05 In depth resource on mechanisms of oxidative stress and damage and the role of free radicals in disease diagnosis and therapeutics *Molecular Basis of Oxidative Stress* is a comprehensive resource on the molecular and chemical bases of oxidative stress providing insight on various diseases caused by oxidative stress cancer cardiovascular neurodegenerative and the role of reactive oxygen species ROS in disease pathogenesis along with in depth knowledge about the mechanisms of oxidative stress and damage free radical chemistry and the role of free radicals in disease diagnosis and therapeutics Thoroughly updated and expanded to reflect advances in the years since its original publication the Second Edition includes new chapters covering topics like oxidative stress mechanisms biomarkers and therapeutic strategies in the management and treatment of diseases The disease section features 10 new emerging diseases including kidney and eye diseases and COPD This Second Edition also covers developments in the field in the last several years such as an increase in mortality rate from air pollution and obstructive pulmonary diseases in which exogenous oxidants are initiators Written by a team of highly qualified academics *Molecular Basis of Oxidative Stress* discusses sample topics including Classification physico chemical properties sources and detection of reactive species and etiology of COPD from cigarette smoke and pollution Oxidative reductive and indirect non redox modifications of key biomolecular systems such as lipids proteins and DNA by reactive species Gene expression of antioxidant defense enzymes mitochondrial dysfunction and aberrant activation of NOX and cell signaling Biomarkers of oxidative stress in neurodegenerative diseases and emerging fields in biomarker discovery such as cysteinylated albumin and nitroalkene fatty acids Imparting strong foundational knowledge of redox chemistry chemistry of oxidative damage and mechanisms of oxidative stress and oxidative stress mediated disease pathogenesis *Molecular Basis of Oxidative Stress* is an essential reference for both novice and advanced toxicologists biochemists and pharmacologists along with clinical and medical scientists in various fields such as oncology cardiovascular and neuroscience

Free Radicals Gerald M. Rosen, 1999-12-02 Free radicals play key roles in physiologic regulation and in many degenerative and pathologic processes making them a fertile area of research This book focuses on spin trapping a sophisticated technique for the

identification of free radicals in biological systems The method is complex and this book offers an in depth guide to all of the critical aspects needed for its application to free radicals in biology This includes advice on interpreting results trouble shooting and experimental designs *The Chemistry of Radical Polymerization* Graeme Moad,D.H. Solomon,2006 This book commences with a general introduction outlining the basic concepts of radical polymerization This is followed by a chapter on radical reactions that is intended to lay the theoretical ground work for the succeeding chapters on initiation propagation and termination

Organic Mechanisms Reinhard Bruckner,2010-04-30 Much of life can be understood in rational terms if expressed in the language of chemistry It is an international language a language without dialects a language for all time a language that explains where we came from what we are and where the physical world will allow us to go Chemical Language has great esthetic beauty and links the physical sciences to the biological sciences from *The Two Cultures Chemistry and Biology* by Arthur Kornberg Nobel Prize in Physiology and Medicine 1959 Over the past two centuries chemistry has evolved from a relatively pure disciplinary pursuit to a position of central importance in the physical and life sciences More generally it has provided the language and methodology that has unified integrated and indeed molecularized the sciences shaping our understanding of the molecular world and in so doing the direction development and destiny of scientific research The language of chemistry referred to by my former Stanford colleague is made up of atoms and bonds and their interactions It is a system of knowledge that allows us to understand structure and events at a molecular level and increasingly to use that understanding to create new knowledge and beneficial change The words on this page for example are detected by the eye in a series of events now generally understood at the molecular level

Handbook of Fullerene Science and Technology Xing Lu,Takeshi Akasaka,Zdeněk Slanina,2022-09-24 Nanocarbon chemistry and physics is a fast developing broad research area the Nobel prizes in 1996 and 2010 awarded to two key discoveries in the field and several other nanocarbon achievements of comparable importance Owing to this rapid growth the nanocarbon landscape fundamentally changes every few years creating a need to survey the field on a regular basis to update the books that have become incomplete or even obsolete As such this book focuses on fullerenes and metallofullerenes and also on the related areas of nanotubes and graphenes All the covered research topics provide important fundamental knowledge for the natural sciences but also for applications in molecular electronics superconductivity catalysis photovoltaics and medical diagnostics The current nanocarbon research activities have particularly high application potential in the conversion of solar energy future molecular memories non conventional materials for optoelectronics and new treatments for civilization diseases Offering a truly up to date critical survey of nanocarbon science its concepts and highlights it follows the concept of a handbook it addresses key topics systematically from historical background methodological aspects current important issues and application potential all supplied with extensive referencing With individual chapters written by leading experts with extensive research experience it is a comprehensive reference resource for graduate students and active researchers alike

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Table of Contents S Centered Radicals

1. Understanding the eBook S Centered Radicals
 - The Rise of Digital Reading S Centered Radicals
 - Advantages of eBooks Over Traditional Books
2. Identifying S Centered Radicals
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an S Centered Radicals
 - User-Friendly Interface
4. Exploring eBook Recommendations from S Centered Radicals
 - Personalized Recommendations
 - S Centered Radicals User Reviews and Ratings
 - S Centered Radicals and Bestseller Lists
5. Accessing S Centered Radicals Free and Paid eBooks
 - S Centered Radicals Public Domain eBooks
 - S Centered Radicals eBook Subscription Services
 - S Centered Radicals Budget-Friendly Options
6. Navigating S Centered Radicals eBook Formats

- ePub, PDF, MOBI, and More
- S Centered Radicals Compatibility with Devices
- S Centered Radicals Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of S Centered Radicals
 - Highlighting and Note-Taking S Centered Radicals
 - Interactive Elements S Centered Radicals
- 8. Staying Engaged with S Centered Radicals
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers S Centered Radicals
- 9. Balancing eBooks and Physical Books S Centered Radicals
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection S Centered Radicals
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine S Centered Radicals
 - Setting Reading Goals S Centered Radicals
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of S Centered Radicals
 - Fact-Checking eBook Content of S Centered Radicals
 - Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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