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C-Винилирование кетонов ацетиленами в основных средах: синтез β,γ -этиленовых кетонов и их синтетическое применение

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The Stetter reaction: modern methodologies and useful applications in total synthesis of natural products and drugs

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The Stetter reaction, a powerful umpolung strategy using the catalysis with nucleophilic carbenes, enables the formation of 1,4-dicarbonyl compounds through the conjugate addition of aldehydes to Michael acceptors. Since its discovery in the 1970s, this reaction has evolved through thiazolium, triazolium, and many more catalysts, and more recently, with chiral *N*-heterocyclic carbenes for asymmetric applications. This review discusses modern advances in the Stetter reaction under green conditions, enzyme catalysis, photochemical activation, and ball-milling techniques. It integrates recent advances in green chemistry, solvent-free systems, and biocatalytic processes while correlating them with applications in the total synthesis of natural products and pharmaceuticals. Particular focus is placed on the evolution of chiral NHCs, artificial Stetterases, and photoinduced pathways, which expand the reaction's utility in asymmetric and sustainable syntheses. These methodologies highlight the reaction's versatility in constructing complex compounds, its environmental compatibility via aqueous or solvent-free conditions, and its ever-growing role in medicinal chemistry. Bibliography — 140 references.

Ring-opening reactions of nitrogen-containing heterocyclic compounds at the nitrogen–heteroatom bond

RCR5202

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For the first time, published data on ring-opening reactions of heterocyclic compounds occurring via the nitrogen–heteroatom bond and resulting in acyclic nitrogen-containing polyfunctional compounds, have been systematized. The processes in which nitrogen, sulfur, selenium, phosphorus and silicon act as heteroatoms are considered. The transformations are analyzed, classified according to the type of reagent that promotes the cleavage of the specified bond, as well as the nature of the heteroatom. Examples of practical use of the resulting compounds are given.

Bibliography — 154 references.

Advances of chemistry for the design of antimicrobial biomaterials

RCR5205

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Despite the substantial progress in the understanding of bactericidal mechanisms and the development of novel antimicrobial strategies, infections remain a major threat for the humankind. It is symptomatic that antibiotic-resistant bacterial infections are now the third most common cause of death, being inferior only to stroke and coronary heart disease. Another increasingly serious threat is posed by fungal infections, especially for hospitalized patients with immunodeficiency or those who recover from COVID-19. The main feature of this review is that it provides a unified systematic view on the control of pathogenic microorganisms. The review begins with a historical account and setting of relevant tasks for innovative medical materials and proceeds with a profound analysis of fundamental mechanisms and advanced solutions. The analysis focuses on the key strategies for controlling bacterial and fungal infections, which are considered in detail in relation to metallic and polymeric biomaterials, inorganic nanoparticles

and heterogeneous platforms based on them for local therapy. Particular attention is paid to factors that regulate the release of ions and therapeutic agents, generation of reactive oxygen species, and synergistic effects involved in these processes. The review also addresses the antibacterial mechanisms of action of nanoparticles and metal-containing complexes, nanoparticle toxicity and ways to minimize it, and bacterial defence mechanisms against ions and nanoparticles. The achievements of modern chemistry related to surface functionalization and immobilization of therapeutic agents aimed at developing highly effective antimicrobial surfaces are demonstrated. Critical analysis of drawbacks of the existing models for *in vitro* and *in vivo* assays of the antibacterial activity of biomaterials is given.

Bibliography — 361 references.

Base-mediated C-vinylation of ketones with alkynes: synthesis of β,γ -ethylenic ketones and their synthetic applications

RCR5206

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This review summarizes the latest advances in the chemistry of β,γ -ethylenic ketones, which have emerged over the last decade as valuable synthetic building blocks to create molecules of high complexity and diversity. This family of multifunctional γ -aryl- β,γ -ethylenic ketones has now become accessible owing to the discovery and systematic development of a new general $C(sp^3)-C(sp^2)$ bond-forming reaction, namely superbse-mediated C-vinylation of ketones with alkynes. In the context of the Favorsky reaction (the addition of acetylenic carbanions to the carbonyl group of ketones), this discovery represents a chemical paradox in the form of temperaturecontrolled inversion of electrophilicity and nucleophilicity of acetylenes and ketones. Various transformations of β,γ -ethylenic ketones: nucleophilic addition reactions, inverse-electron-demand Diels–Alder reactions, reactions involving a carbonyl group followed by transformations of functionalized adducts, *etc.* are discussed. The review also highlights the cascade reactions, in which the *in situ* formed β,γ -ethylenic ketones, are key intermediates in the synthesis of various highly functionalized carbo- and heterocyclic systems.

Bibliography — 102 references.

