

## PROGRAMMA DEL CORSO DI CHIMICA ORGANICA 2

### TESTI ADOTTATI

- Chimica Organica – P. Y. Bruice – 3<sup>a</sup> Ed. EdISES (include un kit di modelli molecolari).
- Organic Chemistry – J. Clayden, N. Greeves, and S. Warren – 2<sup>nd</sup> Ed. Oxford University Press.

### MODULO 1. COMPOSTI BIOORGANICI

#### 20. LA CHIMICA ORGANICA DEI CARBOIDRATI

Classificazione dei carboidrati – La notazione D e L – Configurazione degli aldosi – Configurazione dei chetosi – Reazioni dei monosaccaridi in soluzione basica – Reazioni di ossido-riduzione dei monosaccaridi – Allungamento della catena: la sintesi di *Kiliani-Fischer* modificata (*Serianni-Barker*) – Accorciamento della catena: la degradazione di *Wohl* – I monosaccaridi formano emiacetali ciclici – Il glucosio è il più stabile fra gli aldoesosi – Formazione di glicosidi – L'effetto anomero – Zuccheri riducenti e non riducenti – **Formazione di Eteri, Esteri ed Acetali Ciclici – Agliconi** – Disaccaridi – Polisaccaridi.

➤ *Paragrafi: 20.1–20.8 e 20.10–20.16; appunti di lezione*

#### 21. AMMINOACIDI, PEPTIDI E PROTEINE

Nomenclatura degli amminoacidi – Configurazione degli amminoacidi – Proprietà acido-basiche degli amminoacidi – Il punto isoelettrico – Separazione degli amminoacidi – Metodi di sintesi degli amminoacidi – Risoluzione di una miscela racemica di amminoacidi – Legami peptidici e legami disolfuro – Alcuni peptidi interessanti – Strategie di sintesi peptidica – Sintesi peptidica automatizzata – Introduzione alla struttura delle proteine – Come determinare la struttura primaria di un polipeptide o di una proteina.

➤ *Paragrafi: 21.1–21.13*

### MODULO 2. ARGOMENTI SPECIALI

#### 27. POLIMERI DI SINTESI

Esistono due classi principali di polimeri di sintesi – Introduzione ai polimeri per crescita a catena – Polimerizzazione radicalica – Il teflon: una scoperta accidentale – Codici di riciclo – Polimerizzazione cationica – Polimerizzazione anionica – Polimerizzazione con apertura d'anello – Stereochimica della polimerizzazione • catalizzatori di *Ziegler-Natta* – Polimerizzazione dei dieni – Copolimeri – Introduzione ai polimeri per crescita a stadi – Classi di polimeri per crescita a stadi – Progettare un polimero – Proprietà fisiche dei polimeri – Il riciclo dei polimeri – Polimeri biodegradabili.

➤ *Paragrafi: 27.1–27.14*

#### 8/28/34/35. REAZIONI PERICICLICHE

Le tre tipologie di reazioni pericicliche: Reazioni elettrocicliche, di cicloaddizione e trasposizioni sigmatropiche – Orbitali molecolari e simmetria degli orbitali – Reazioni elettrocicliche – Reazioni di cicloaddizione – Trasposizioni sigmatropiche – **Elettrociclic reactions in detail – A new sort of reaction – General description of the *Diels-Alder* reaction** – Reazione di *Diels-Alder*: una reazione di addizione 1,4 – Analisi retrosintetica della reazione di *Diels-Alder* – **The frontier orbital description of cycloadditions – Regioselectivity in *Diels-Alder* reactions – The *Woodward-Hoffmann* description of the *Diels-Alder* reaction – Trapping reactive intermediates by cycloadditions – Other thermal cycloadditions – Photochemical [2 + 2] cycloadditions – Thermal [2 + 2] cycloadditions – Making**

five-membered rings: 1,3-dipolar cycloadditions – Sigmatropic rearrangements – Orbital descriptions of [3,3]-sigmatropic rearrangements – The direction of [3,3]-sigmatropic rearrangements – [2,3]-Sigmatropic rearrangements – Sigmatropic hydrogen and alkyl shifts – Electrocyclic reactions.

➤ *Paragrafi: 8.14, 8.15 e 28.1–28.5; Chapters 34 and 35; appunti di lezione*

### 36. PARTICIPATION, REARRANGEMENT, AND FRAGMENTATION

Neighbouring groups can accelerate substitution reactions – Rearrangements occur when a participating group ends up bonded to a different atom – Carbocations readily rearrange – The pinacol rearrangement – The dienone-phenol rearrangement – The benzylic acid rearrangement – The *Favorskii* rearrangement – Migration to oxygen: the *Baeyer–Villiger* reaction – The *Beckmann* rearrangement – Polarization of C–C bonds helps fragmentation – Fragmentations are controlled by stereochemistry – Ring expansion by fragmentation – Controlling double bonds using fragmentation.

### 11/38. SYNTHESIS AND REACTIONS OF CARBENES

Diazomethane makes methyl esters from carboxylic acids – Photolysis of diazomethane produces a carbene – How do we know that carbenes exist? – Ways to make carbenes – Carbenes can be divided into two types – How do carbenes react? – Carbenes react with alkenes to give cyclopropanes – Insertion into C–H bonds – Rearrangement reactions – Nitrenes are the nitrogen analogues of carbenes – Alkene e alchini metathesis.

➤ *Paragrafo: 11.5; Chapter 38*

### 11/40. ORGANOMETALLIC CHEMISTRY OF PALLADIUM, BORON, TIN, RHODIUM, AND RUTHENIUM

Reazioni di accoppiamento catalizzate da palladio – *Grubbs*, *Schrock*, *Suzuki* ed *Heck* ricevono il premio Nobel – Transition metals extend the range of organic reactions – The 18 electron rule – Bonding and reactions in transition metal complexes – Palladium is the most widely used metal in homogeneous catalysis – The *Heck* reaction couples together an organic halide or triflate and an alkene – Cross-coupling of organometallics and halides – Allylic electrophiles are activated by palladium(0) – Palladium-catalysed amination of aromatic rings – Alkenes coordinated to palladium(II) are attacked by nucleophiles – Palladium catalysis in the total synthesis of a natural alkaloid – An overview of some other transition metals.

➤ *Paragrafo: 11.4; Chapter 40*

### 39. DETERMINING REACTION MECHANISMS

There are mechanisms and there are mechanisms – Determining reaction mechanisms: the *Cannizzaro* reaction – Be sure of the structure of the product – Systematic structural variation – The *Hammett* relationship – Other kinetic evidence for reaction mechanisms – Acid and base catalysis – The detection of intermediates – Stereochemistry and mechanism – Summary of methods for the investigation of mechanism.

## MODULO 3. RETROSINTESI E STEREOSELETTIVITÀ

### 28. RETROSYNTHETIC ANALYSIS

Creative chemistry – Retrosynthetic analysis: synthesis backwards – Disconnections must correspond to known, reliable reactions – Synthons are idealized reagents – Multiple step syntheses: avoid chemoselectivity problems – Functional group interconversion – Two-group disconnections are better than one-group disconnections – C–C disconnections – Available starting materials – Donor and acceptor synthons – Two-group C–C disconnections – 1,5-Related functional groups – “Natural reactivity” and “umpolung”.

### **31. SATURATED HETEROCYCLES AND STEREOELECTRONICS**

Introduction – Reactions of saturated heterocycles – Conformation of saturated heterocycles: Heteroatoms in rings have axial and equatorial lone pairs – Some substituents of saturated heterocycles prefer to be axial: the anomeric effect – The anomeric effect in spiroketals – Related effects in other types of compounds – Making heterocycles: ring-closing reactions – Diastereotopic groups.

### **32. STEREOSELECTIVITY IN CYCLIC MOLECULES**

Introduction – Stereochemical control in six-membered rings – Reactions on small rings – Regiochemical control in cyclohexene epoxides – Stereoselectivity in bicyclic compounds – Fused bicyclic compounds – Spirocyclic compounds – Reactions with cyclic intermediates or cyclic – transition states.

### **33. DIASTERESELECTIVITY**

Looking back – Prochirality – Additions to carbonyl groups can be diastereoselective even without rings – Stereoselective reactions of acyclic alkenes – Aldol reactions can be stereoselective – Single enantiomers from diastereoselective reactions.

### **41. ASYMMETRIC SYNTHESIS**

Nature is asymmetric – The chiral pool: Nature’s chiral centres “off the shelf” – Resolution can be used to separate enantiomers – Chiral auxiliaries – Chiral reagents – Asymmetric catalysis – Asymmetric formation of carbon–carbon bonds – Asymmetric aldol reactions.