Understanding Advanced Organic and Analytical Chemistry

The Learner's Approach

This page intentionally left blank

Understanding Advanced Organic and Analytical Chemistry

The Learner's Approach

Kim Seng Chan

BSc (Hons), PhD, PGDE (Sec), MEd, MA (Ed Mgt), MEd (G Ed)

Jeanne Tan

BSc (Hons), PGDE (Sec), MEd (LST)

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

UNDERSTANDING ADVANCED ORGANIC AND ANALYTICAL CHEMISTRY The Learners' Approach

Copyright © 2012 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN-13 978-981-4374-98-9 (pbk)

ISBN-10 981-4374-98-9 (pbk)

Typeset by Stallion Press

Email: enquiries@stallionpress.com

Printed in Singapore.

Preface

The majority of the learning of organic chemistry in classrooms happens with the help of textbooks and lecture notes. Unfortunately, most textbooks are of the expository and non-refutational type, presenting facts rather than explaining them. In addition, the links between concepts are often not made explicit, presupposing that learners would be able to make the necessary integration with the physical chemistry concepts they have come across, forgetting that some learners lack the prior knowledge and metacognitive skills to do so. Hence, learners would at most be able to reproduce the information that is structured and organized by the textbook writer, but not able to construct a meaningful conceptual mental model for oneself.

This current book is a continuation of our first book, *Understanding Advanced Physical Inorganic Chemistry*, retaining the main refutational characteristics of the first book by strategically planting think-aloud questions to promote conceptual understanding, knowledge construction and discourse opportunities. It is hoped that these essential questions will make learners aware of the possible conflict between their prior knowledge, which may be counter intuitive or misleading with those presented in the text, and hence in the process, make the necessary conceptual changes. In essence, we are trying to effect metaconceptual awareness — awareness of the theoretical nature of one's thinking — while learners are trying to master organic chemistry concepts. We hope that by pointing out the differences between possible misconceptions and the actual chemistry content, we can promote metaconceptual awareness and thus assist

the learner in constructing a meaningful conceptual model of understanding for organic chemistry. We want our learners to not only know what they know, but at the same time have a sense of how they know what they know, and how their new learning is interrelated within the discipline.

Lastly, the substance of this book would be both informative and challenging to the practices of teachers. This book would certainly illuminate the teaching of all chemistry teachers that strongly believe in teaching organic chemistry with a meaningful and integrative approach, from the learners' perspective. The integrated questions at the end of each chapter will certainly prove useful to students in helping them to revise fundamental concepts learnt from previous chapters and also to see the importance and relevance in the application to their current learning. Collectively, this book offers a vision of understanding organic chemistry meaningfully and fundamentally from the learners' approach and to fellow chemistry teachers, we hope that it will help you develop a greater insight into what makes you tick, explain, enthuse and develop in the course of your teaching.

Acknowledgements

We would like to express our sincere thanks to the staff at World Scientific Publishing Co. Pte. Ltd. for the care and attention which they have given to this book, particularly our editors Lim Sook Cheng and Sandhya Devi, our editorial assistant Chow Meng Wai and Stallion Press.

We also wish to take this opportunity to express our gratitude to Yeo Yam Khoon of Raffles Institution (Year 5–6) who has been and will always be an inspiration for his unwavering commitment to the teaching of chemistry. Special thanks to Tham Zisheng of Raffles Institution (Year 5–6) for some of his invaluable suggestions.

Special thanks go to all our students who have made our teaching of chemistry fruitful and interesting. We have learnt a lot from them just as they have learnt some good chemistry from us.

Finally, we thank our families for their wholehearted support and understanding throughout the period of writing this book.

This page intentionally left blank

Contents

Preface	v
Acknowledgements	vii
1. Structure and Bonding	1
1.1 Introduction	1
1.2 Structural Formulae of Organic Compounds . . .	3
1.3 Bonding and Shapes of Organic Molecules	6
1.3.1 sp^3 Hybridization	8
1.3.2 sp^2 Hybridization	9
1.3.3 sp Hybridization	11
1.3.4 Delocalized Bonding/Resonance	13
1.4 Bonding and Reactivity of Organic Compounds	15
1.4.1 Nature and Strength of Covalent Bonds	15
1.4.2 Types of Intermolecular Attractive Forces	18
1.4.3 Bonding and Physical Properties of Organic Compounds	22
2. Isomerism in Organic Compounds	29
2.1 Introduction	29
2.2 Structural Isomerism	30
2.2.1 Chain Isomerism	30

2.2.2	Positional Isomerism	31
2.2.3	Functional Group Isomerism	34
2.3	Stereoisomers	35
2.3.1	Geometrical Isomerism (<i>cis-trans</i> Isomerism)	37
2.3.2	Conformational Isomerism	43
2.3.3	Optical Isomerism	46
3.	Organic Reactions and Mechanisms	61
3.1	Introduction	61
3.2	Types of Bond Cleavage	67
3.2.1	Homolytic Bond Cleavage	68
3.2.2	Heterolytic Bond Cleavage	69
3.2.3	Type of Reaction Intermediates	70
3.3	Types of Organic Reactions	73
3.3.1	Rearrangement Reactions	74
3.3.2	Redox Reactions	74
3.3.3	Addition Reactions	74
3.3.4	Elimination Reactions	75
3.3.5	Substitution Reactions	76
3.4	Types of Reaction Mechanisms	76
3.4.1	Electrophilic Addition Mechanism	77
3.4.2	Nucleophilic Addition Mechanism	81
3.4.3	Free Radical Substitution Mechanism	86
3.4.4	Electrophilic Substitution Mechanism	88
3.4.5	Nucleophilic Substitution Mechanism	92
4.	Alkanes	105
4.1	Introduction	105
4.2	Nomenclature	106
4.3	Physical Properties	110
4.3.1	Melting and Boiling Points	110
4.3.2	Solubility	112
4.4	Preparation Methods	112
4.4.1	Catalytic Hydrogenation of Alkenes	112
4.5	Chemical Properties	113
4.5.1	Combustion — Oxidation	113

4.5.2	Halogenation — Free Radical Substitution	115
4.5.3	Thermal and Catalytic Cracking	119
5.	Alkenes	123
5.1	Introduction	123
5.2	Nomenclature	123
5.3	Physical Properties	127
5.3.1	Melting and Boiling Points	127
5.3.2	Solubility	130
5.4	Preparation Methods	130
5.4.1	Dehydration of Alcohols	130
5.4.2	Dehydrohalogenation of Halogenoalkanes	132
5.5	Chemical Properties	133
5.5.1	Catalytic Hydrogenation — Reduction	133
5.5.2	Formation of Halogenoalkane — Electrophilic Addition	135
5.5.3	Formation of Dihalide — Electrophilic Addition	139
5.5.4	Formation of Halohydrin — Electrophilic Addition	139
5.5.5	Formation of Alcohol — Electrophilic Addition	142
5.5.6	Combustion — Oxidation	144
5.5.7	Formation of Diol — Oxidation	144
5.5.8	Formation of Carbon Dioxide, Ketone and Carboxylic Acid — Oxidation	145
5.5.9	Formation of Aldehyde and Ketone — Oxidation	148
5.6	Summary	149
6.	Arenes	153
6.1	Introduction	153
6.2	Nomenclature	158
6.3	Physical Properties	159

6.3.1	Melting and Boiling Points	159
6.3.2	Solubility	159
6.4	Chemical Properties of Benzene	160
6.4.1	Formation of Halogenoarene — Electrophilic Substitution	160
6.4.2	Formation of Alkylbenzene — Electrophilic Substitution	161
6.4.3	Formation of Nitrobenzene — Electrophilic Substitution	163
6.4.4	Catalytic Hydrogenation — Reduction	165
6.4.5	Combustion — Oxidation	166
6.5	Benzene Derivatives	166
6.5.1	The Influence of the Substituent on the Rate of Electrophilic Substitution	166
6.5.2	The Influence of the Substituent on the Orientation of Electrophilic Attack	171
6.6	Chemical Properties of Methylbenzene	175
6.6.1	Formation of Halogenoarene — Electrophilic Substitution	175
6.6.2	Formation of Alkyl(Methylbenzene) — Electrophilic Substitution	176
6.6.3	Formation of Nitroarene — Electrophilic Substitution	176
6.6.4	Halogenation — Free Radical Substitution (at Alkyl Side-Chain)	179
6.6.5	Formation of Benzoic Acid — Oxidation (at Alkyl Side-Chain)	180
6.7	Summary	182
7.	Halogen Derivatives	185
7.1	Introduction	185
7.2	Nomenclature	185
7.3	Physical Properties	187
7.3.1	Melting and Boiling Points	187
7.3.2	Solubility	188

7.4	Preparation Methods for Halogenoalkanes	188
7.4.1	Nucleophilic Substitution of Alcohols . .	188
7.4.2	Formation of Halogenoalkane — Electrophilic Addition	189
7.4.3	Formation of Dihalide — Electrophilic Addition	191
7.5	Chemical Properties of Halogenoalkanes	192
7.5.1	Formation of Alcohol — Nucleophilic Substitution	193
7.5.2	Formation of Nitrile — Nucleophilic Substitution	195
7.5.3	Formation of Amine — Nucleophilic Substitution	197
7.5.4	Formation of Ether — Nucleophilic Substitution	200
7.5.5	Formation of Alkene Via Dehydrohalogenation — Elimination . . .	201
7.6	Halogenoalkanes versus Halogenoarenes	204
7.7	Preparation Methods for Halogenoarenes	206
7.7.1	Formation of Halogenoarene — Electrophilic Substitution	206
7.8	Chemical Properties of Halogenoarenes	206
7.8.1	Formation of Benzene Derivatives — Electrophilic Substitution	206
7.9	Summary	207
8.	Alcohols and Phenol	211
8.1	Introduction	211
8.2	Nomenclature	212
8.3	Physical Properties	213
8.3.1	Melting and Boiling Points	213
8.3.2	Solubility	214
8.4	Hydrolysis and Acidity	217
8.5	Preparation Methods for Alcohols	233
8.5.1	Electrophilic Addition of Alkenes	233
8.5.2	Nucleophilic Substitution of Halogenoalkanes	234

8.5.3	Reduction of Carboxylic Acids and Carbonyl Compounds	234
8.6	Chemical Properties of Alcohols	235
8.6.1	Acid-Base Reaction with Strong Bases and Reactive Metals	235
8.6.2	Formation of Esters with Carboxylic Acids — Esterification via Nucleophilic Substitution	237
8.6.3	Formation of Esters with Acid Chlorides — Acylation via Nucleophilic Substitution	239
8.6.4	Formation of Alkenes — Dehydration . .	240
8.6.5	Formation of Halogenoalkanes — Nucleophilic Substitution	243
8.6.6	Formation of Carbonyl Compounds and Carboxylic Acids — Oxidation . . .	245
8.6.7	Formation of Tri-Iodomethane (Iodoform) — Oxidation	249
8.7	Chemical Properties of Phenol	250
8.7.1	Acid-Base Reaction with Strong Bases and Reactive Metals	251
8.7.2	Formation of Esters with Acid Chlorides — Acylation	251
8.7.3	Formation of Halogenophenol — Electrophilic Substitution	252
8.7.4	Formation of Nitrophenol — Electrophilic Substitution	254
8.7.5	Test for Phenol	255
8.8	Summary	256
9.	Carbonyl Compounds	261
9.1	Introduction	261
9.2	Nomenclature	262
9.3	Physical Properties	262
9.3.1	Melting and Boiling Points	262
9.3.2	Solubility	263

9.4	Preparation Methods for Carbonyl Compounds	264
9.4.1	Oxidation of Alcohols	264
9.4.2	Oxidation of Alkenes	264
9.4.3	Ozonolysis — Oxidation of Alkenes . . .	265
9.5	Chemical Properties of Carbonyl Compounds	265
9.5.1	Formation of Cyanohydrins — Nucleophilic Addition	266
9.5.2	Condensation Reaction (Addition–Elimination Reaction)	267
9.5.3	Formation of Carboxylic Acid — Oxidation	270
9.5.4	Formation of Carboxylate Salts Using Tollen's Reagent — Oxidation	271
9.5.5	Formation of Carboxylate Salts using Fehling's Reagent — Oxidation of Aliphatic Aldehydes	273
9.5.6	Formation of Tri-Iodomethane (Iodoform) — Oxidation	275
9.5.7	Formation of Alcohols — Reduction . . .	277
9.6	Aromatic Carbonyl Compounds	279
9.7	Summary	280
10.	Carboxylic Acids and Their Derivatives	287
10.1	Introduction	287
10.2	Nomenclature	287
10.3	Physical Properties	288
10.3.1	Melting and Boiling Points	288
10.3.2	Solubility	291
10.4	Preparation Methods for Carboxylic Acids	291
10.4.1	Oxidation of Primary Alcohols	291
10.4.2	Oxidation of Aldehydes	291
10.4.3	Oxidation of Alkenes	292
10.4.4	Hydrolysis of Nitriles	292
10.4.5	Oxidation of Alkylbenzene	293

10.5	Chemical Properties of Carboxylic Acids	293
10.5.1	Acid–Base Reaction with Strong Bases and Reactive Metals	295
10.5.2	Formation of Acyl Chlorides — Nucleophilic Substitution	296
10.5.3	Formation of Esters with Alcohols — Esterification via Nucleophilic Substitution	297
10.5.4	Reduction of Carboxylic Acids to Primary Alcohols	297
10.6	Derivatives of Carboxylic Acids	298
10.6.1	Nomenclature	299
10.6.2	Physical Properties	299
10.6.3	Chemical Properties	300
10.6.4	Chemistry of Acid Chlorides	302
10.6.5	Chemistry of Esters	307
10.6.6	Chemistry of Amides	310
10.7	Summary	312
11.	Amines	321
11.1	Introduction	321
11.2	Nomenclature	321
11.3	Physical Properties	322
11.3.1	Melting and Boiling Points	322
11.3.2	Solubility	324
11.3.3	Basicity	324
11.4	Preparation Methods for Amines	328
11.4.1	Nucleophilic Substitution of Halogenoalkanes	328
11.4.2	Reduction of Amides	329
11.4.3	Reduction of Nitriles	329
11.4.4	Reduction of Nitrobenzene	330
11.5	Chemical Properties	331
11.5.1	Acid–Base Reaction with Acids	331
11.5.2	Formation of Amides with Acid Chloride — Acylation via Nucleophilic Substitution	332

11.5.3	Formation of Amides with Esters — Nucleophilic Substitution	332
11.5.4	Formation of Amine — Nucleophilic Substitution	333
11.5.5	Formation of Halogenophenylamine — Electrophilic Substitution	334
11.5.6	Reaction of Primary Amine with Nitrous Acid	336
11.6	Summary	336
12.	Amino Acids	341
12.1	Introduction	341
12.2	The Formation of Zwitterions — An Intramolecular Acid–Base Reaction	347
12.3	Physical Properties of Zwitterions	349
12.3.1	Melting and Boiling Points	349
12.3.2	Solubility	349
12.4	Chemical Properties of Zwitterions	350
12.4.1	Acid–Base Reaction with Acids or Bases	350
12.4.2	Formation of Amides	359
12.4.3	Polymerization — Reaction between Amino Acids	360
13.	Polymers	363
13.1	Introduction	363
13.2	Addition Polymers	368
13.2.1	Free Radical Polymerization of Alkene . .	368
13.2.2	Types of Addition Polymers and Their Properties	371
13.2.3	Pollution Problems Associated with Poly(Alkenes)	379
13.3	Condensation Polymers	379
13.3.1	Polyesters	380
13.3.2	Polyamides	381
13.4	Biological Polymers — Polypeptides and Proteins	384

13.4.1	The Different Levels of Protein Structure	387
13.4.2	Denaturation of Proteins	395
14.	Mass Spectrometry	405
14.1	Introduction	405
14.2	Basic Features of a Mass Spectrometer	407
14.3	Mass Spectrum Analysis	410
14.4	Analyzing the Mass Spectrum of an Element	414
14.5	Analyzing the Mass Spectrum of Alkanes	417
14.6	Analyzing the Mass Spectrum of Chloroalkanes	422
14.7	Analyzing the Mass Spectra of Isomers	425
14.8	Deducing the Structure of an Unknown Compound from Mass Spectrum Analysis	430
15.	Ultra-Violet and Visible Spectroscopy	433
15.1	Introduction	433
15.2	Molecular Orbital Theory (MO Theory)	436
15.3	Basic Principles of Spectroscopy	445
15.4	Types of Spectroscopic Methods	450
15.4.1	Ultraviolet–Visible (UV-Vis) Spectroscopy	451
16.	Infrared Spectroscopy	457
16.1	Introduction	457
16.2	What is the Concept of Degree of Freedom?	462
16.3	How is an IR Spectrum for a Molecule Determined?	465
16.4	Analyzing the IR Spectrum of Simple Molecules	466
16.5	Analyzing the IR Spectrum of Organic Molecules	468
17.	Nuclear Magnetic Resonance Spectroscopy	477
17.1	Introduction	477

17.2	Principal of ^1H NMR Spectroscopy	483
17.3	How Is a ^1H NMR Spectrum for a Molecule Determined?	485
17.3.1	Chemical Shifts	488
17.3.2	Factors that Account for the Relative Chemical Shifts	491
17.4	Important Features on the ^1H NMR Spectrum of Organic Molecules	496
17.4.1	The Number of Signals	497
17.4.2	The δ Value of Each Signal	497
17.4.3	The Relative Areas under the Peaks . . .	498
17.4.4	The Splitting Patterns of the Signals . .	500
17.5	Analyzing the ^1H NMR Spectrum of Simple Organic Molecules	507
17.6	Labile Protons and Proton Exchange Reactions	510
18.	Chromatography and Electrophoresis	513
18.1	Introduction	513
18.2	Paper Chromatography — An Introduction to Chromatography Technique	514
18.3	Thin Layer Chromatography (TLC)	520
18.4	Column Chromatography (CC)	522
18.5	High-Performance Liquid Chromatography (HPLC)	523
18.6	Gas-Liquid Chromatography (GLC)	524
18.7	Electrophoresis	525
	Index	527