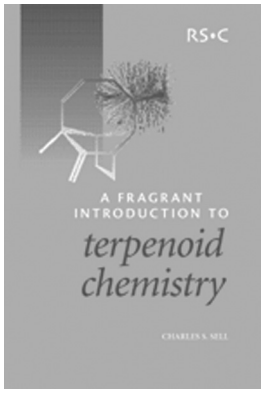
*Michael H. Benn**



A Fragrant Introduction to Terpenoid Chemistry

by Charles S. Sell
RSC, Cambridge
2004, 414 pp
ISBN 0-85404-681-X
Softcover, £50

In this text, more idiosyncratic than most, the author uses the niche chemical industry of perfumes and odorants as a framework for a book stated to be 'aimed primarily at university undergraduates, postgraduates and professional chemists who wish to build up there knowledge of terpene chemistry', although the style suggests that the focus is really on the first group. Did he succeed?

Of the ten chapters the first (Background) defines terpenes by the old Wallach isoprene rule (no mention of Ruzicka's biogenic version), and sketches the roles played by terpenes in nature as well as procedures used in perfumery for their isolation. The second (Biosynthesis) presents the terpenes as derived from mevalonate—i.e. does not alert the reader to the non-mevalonate (deoxyxylulose/methylerythritol) pathway, omits any mention of the cyclopropyl compounds (prequalene alcohol diphosphate, etc.) now known to be intermediates in the tail-to-tail coupling of terpene diphosphates, and presents the cyclization of squalene epoxide to lanosterol without attention to the important stereochemical chair–boat–chair folding of the epoxide required in this process (a matter similarly avoided in chapter 5, where the all-*trans*-squalene epoxide is drawn with a conveniently located *cis* double-bond).

Chapter 3 (Linear and Monocyclic Monoterpenoids) outlines classical structure determination by degradation and unambiguous syntheses, as well as introducing carbocation chemistry in the conversion of α-pinene to terpineol. The main theme of chapter 4 (Menthol and Carvone) is stereochemistry, and it begins with a 10-page consideration of isomerism, a truncated version of what is normally covered in the first year of undergraduate studies. Chapter 5 (Bicyclic Monoterpenoids) is largely devoted to the fundamentals of carbocation chemistry, including such golden oldies as the rearrangements of pinene hydrochloride to bornyl chloride and camphene hydrochloride to isobornyl chloride, but an otherwise good treatment is marred by a mildly irritating labelling of the *anti*-periplanar conformation as *trans*-*anti*-periplanar (presumably so as to produce a memorable acronym, TAP), incomplete orbital-explanations for this process and the Prins reaction, and a final section where a diazonium ion is said (and shown) to lose nitrogen to yield a carbene.

Chapter 6 (Precious Woods) exercises principles from earlier chapters using the sandalwood and cedar sesquiterpenes, including the synthesis of synthetic substitutes for perfumery, and covers, among others, *exo*/*endo* selectivity, the Wittig olefination reaction and its Schlosser modification, Robinson annulation, and the Friedel–Crafts alkylation of alkenes. Chapter 7 (Other Woody Odorants) similarly examines the vetivones, rearrangements of santonin, patchouli constituents, longifolene, caryophyllene, and humulene. Like the two preceding chapters this one is generally a good, and thought-provoking read, for example, isn't the reaction shown in 7.3.4, a radical chain process, rather than simple stepwise addition of trichloromethyl and bromine radicals to an alkene? Chapter 8 (Degradation Products) looks at compounds used in perfumery which are derived by the oxidative degradation of terpenes including ambergris, labdanoids, ionones, and damascones. The inclusion here of the degradation of carotenes to vitamin A, and the role of that compound in the visual process (7 pp.), while a fascinating story, struck me as out of place (and anyway, is usually touched on, albeit in less detail, in elementary organic chemistry courses). Chapter 9 (Commercial Production of Terpenoids) lists the requirements for commercial production, and uses citral as a specific example of the evolution of a synthetic process; also included are the Simplex procedure for two-variable (here, time and temperature) optimization of yield, and the development of product trees (utilization of intermediates for the production of other chemicals). Chapter 10 (Discovery and Design of Novel Molecules) considers the generalities of discovering new molecules with desirable properties, doing so using the specific cases of fragrance ingredients, with a diversion (9 pp.) into a discussion of the nature of odours, including the mechanism of olfaction. Usually each chapter has its own brief set of references, but the book finishes with a short general topic-bibliography followed by a set of 34 chapter-related problems and their answers, before concluding with indexes.

The author had the commendable objective of making his readers aware of the historic role of terpenes and chemists working with perfumery constituents in the development of organic chemistry, and has written a book that will surely give most readers some new knowledge of perfume constituents and make them think about some chemical problems. However, the generalization of young scientists as uninterested in the background history of their disciplines is in my experience both true and understandable—their concern is in learning the best tools of theory and practice that will enable them to tackle new problems and mostly consider who did what, where, and why as immaterial. For an undergraduate chemist working with a four-year constraint, their personal library in organic chemistry is best stocked with one of the numerous excellent *Organic Chemistry* texts, such as Carey's, plus something extra perhaps in the form of Fleming's *Frontier*

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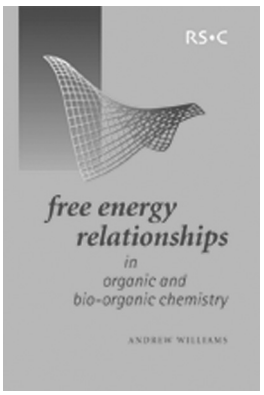
Orbitals and Organic Chemical Reactions. An exposure to natural products, including terpenes, is very desirable, but best done by a course which uses biosynthesis to introduce order, as in Dewick's *Medicinal Natural Products*. *The Fragrant Introduction to Terpene Chemistry* might be an adjunct to such a course, i.e. it would be worth having in a central library. For more advanced readers, with a wealth of source material also available at their fingertips through the Web, I recommend the text, with reservations, as an unusual and interesting read.

Michael Benn is Emeritus Professor at the Department of Chemistry, University of Calgary. His research interests are in biologically active natural products, derived from plants, microorganisms, arthropods, and higher animals.

*Uta Wille**



Free Energy Relationships in Organic and Bio-Organic Chemisty

by Andrew Williams
RSC, Cambridge
2003, 297 pp
ISBN 0-85404-676-3
Softcover, £40

Free energy relationships are the simplest and easiest of techniques to use for studying reaction mechanisms, but the results are often not easy to interpret. Because the most recent undergraduate texts devoted to free energy relationships were published some thirty years ago and applications of free energy relationships to the study of organic and bio-organic reaction mechanisms have undergone substantial transformations since then, this book aims to demonstrate these methods, with a special emphasis on the concepts of *effective charge* and *similarity*, to senior undergraduates and postdoctoral workers engaged in such investigations.

After a general introduction into the physico-chemical origin of free energy relationships in chapter 1, chapter 2 is dedicated to the derivation of the various existing equations, starting with the most familiar, e.g. the Hammett, Taft, and Brønsted equations, followed by those modelling the nucleophilic substitution reaction at an sp^3 carbon (Swain–Scott and Richie equations) and solvent influences on the reactions mechanism (Grunwald–Winstein and Hansch equations). The concept of effective charge, which simplifies the interpretation of the slopes of linear free energy relationships from polar substituent effects (this is relevant, as the linear free energy equations do not directly give charge characteristics of a reaction), is introduced in chapter 3. Chapter 4 is devoted to the description of the transmission of polar substituent effects to a reaction centre, e.g. via σ-inductive, field, or resonance effects, and introduces the various equations, which take these effects into account. Chapter 5 presents formalisms that consider the influence of substituent variation on the slope of the free energy relationship by either cross- or self-interactions. Some anomalies, special cases, and non-linear behaviour are described in chapter 6, whereas chapter 7 presents applications of the various free energy correlations to organic and bio-organic reaction systems. Derivations for selected equations, which were, due to their length not included in the respective chapters, are given in the Appendix, which also contains extensive tables, listing structure and linear free energy parameters. Each chapter contains, besides references, a list of recommended further literature and problems, for which the answers are also given in the Appendix.

This book has positive but also negative aspects. A clear plus is chapter 7 containing the potential applications of free energy correlations for the diagnosis of a mechanism, demonstration of intermediates, parallel reactions, and concerted mechanisms, and which also shows how physico-chemical constants can be calculated and kinetically equivalent mechanisms resolved from linear free energy relationships. Very useful for the potential applicant of this technique is also the compilation of the structure and linear free energy parameters, although the author recommends checking the data against the quoted literature prior to use.

On the other hand, the remaining chapters dealing with the introduction or derivation, respectively, of the various equations might only be understandable to those who are already working in this field. Unfortunately, the extensive use of simplifications and introduction of parameters, often without further or only very poor explanation (the reader is instead referred to the quoted literature) and the prosaic style makes the book very difficult to read, so that potential new users of this technique could be discouraged. In addition to this, the book is not without mistakes: many figures show a logarithm of a rate constant with a unit.

To conclude, this book provides a broad overview about the existing linear free energy equations. With its many literature references, it could prove to be a very useful compilation for students already familiar with this area. However, it cannot be regarded as a textbook providing an inspiring entry into the interesting and important field of free energy relationships as a tool in mechanistic studies, and for those in search of something like that this book cannot be recommended.

**Uta Wille graduated from her PhD in physical chemistry in 1993 and completed a Habilitation in 1999, both at the Universität Kiel. After a postdoctoral stay with Bernd Giese in Basel in 1997/98, she was appointed as a Privatdozent at the Universität Kiel (1999), and in 2003 as a Lecturer at the School of Chemistry at Melbourne University. Her research interests are free-radical reactions in organic and bio-organic chemistry.*

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