(www.interscience.com) DOI 10.1002/aoc.1429

Book Review

GEORGE A. OLAH and DOUGLAS A. KLUMPP

Superelectrophiles and Their Chemistry

John Wiley & Sons; 2007

302 pages; price 99.90 Euro (Hardcover)
ISBN-10: 0-470-04961-8
ISBN-13: 978-0-470-04961-7

The concept of superelectrophilicity emerged in the 1970's, mainly as a consequence of Olah's pioneering work on organic reactivity in superacid solvents such as HF/SbF_5. However, the value of superelectrophilic species in *synthetic* chemistry has been established only within the past decade or so, largely through the work of Klumpp and his associates who have exploited the superacidic but otherwise benign solvent trifluoromethanesulfonic (''triflic'') acid as a medium for the generation of superelectrophiles. It seems fitting that Olah and Klumpp have now collaborated to produce the first comprehensive review of superelectrophile chemistry.

The concept itself is a simple one. On mono-protonation, normally weak electrophiles such as organic carbonyl compounds display greatly increased reactivity towards nucleophiles (especially weak nucleophiles such as unactivated arenes), so that many reactions of carbonyl compounds can only be achieved in the presence of strong acids. It therefore seems reasonable that *multiple* protonation (or coordination to multiple Lewis acid centres) of an electrophile should increase its electrophilic character still further, although it obviously requires a very strong acid to protonate an already positively-charged species. Superacid media, defined as those having an acidity function H_0 significantly more negative than that of 100% sulfuric acid ($H_0 = -12$), are thus generally required to produce multiply-protonated (or any rate mutiply-*charged*) cations, centred on electronegative atoms such as carbon, nitrogen, oxygen, sulfur and chlorine. It is these species, exemplified by doubly protonated 1,2-diketones, protonated acylium ions, the protonated nitronium ion $[O{=}N{=}OH]^{2+}$, and even *triply*-protonated N-chlorosuccinimide, which are the focus of the book.

The first Chapter provides a short, general introduction to superelectrophilicity and its origins, and moves on to an extended discussion of the study of multiply charged superelectrophiles by kinetic, spectroscopic and computational methods. Such species are here classified as either *gitonic* (i.e. with neighbouring positive centres) or *distonic* (where the charge centres are more than three atoms apart), and superelectrophilic activation is shown to diminish as the distance between the charge centres increases. The third Chapter deals with the experimental conditions needed to generate superelectrophiles, and Chapter 4 begins an extended survey, continuing through Chapters 5 and 6, of the structures and reactions of the various types of gitonic electrophile. Chapter 7 covers the structures and organic reactions of distonic species, and the final Chapter reviews briefly the significance of superlectrophilic intermediates in synthetic organic and materials chemistry (novel polycondensation reactions based on superelectrophilic aromatic substitution have recently been discovered, for example).

The central Chapters of the book provide an extremely detailed survey of the role of superelectrophilic activation in organic chemistry, where it enables electrophilic aromatic substitution of unactivated and even *de*activated arenes by a wide range of nominally ''weak'' electrophiles, whose reactivity is multiplied manyfold in superacid media. Other types of reactions are also described however, including ''ionic'' reduction of arenes through sequential protonation and hydride abstraction from very weak hydride donors such as cycloalkanes.

The book is remarkably free of errors (apart from a couple of orphan references on the final page) and is produced to a very high standard. It is an excellent - and so far unique - source of reference to an area of organic chemistry which is just opening up for widespread synthetic applications, and can be strongly recommended to chemists with interests in both preparative and mechanistic organic chemistry.

Howard Colquhoun
University of Reading Reading, UK