

courses in environmental law, planning and science. I have my doubts as to whether the lawyers will understand all of it; the analytical chapter, for example, will not be easily followed by those without a chemistry background. For this latter market, though, the book is generally successful; but perhaps even more usefully, it provides a source of information for the laboratory worker to see some of the 'real world' consequences of his/her toxicity or analytical studies.

The work is multi-authored by distinguished workers in the TBT field. In general, it is sensibly divided into chapters concerned with the manufacture, analysis, occurrence, fate and toxicity/biological aspects. The last two chapters discuss legislative and other legal aspects. The first chapter, by the editor, sets out the pros and cons of TBT use in the antifouling area. The chapter on manufacture (41 pages) is probably rather long for the bulk of the readership. My only structural criticism of the work is the existence of some overlap in Chapters 4–6, particularly in the fate and toxicity areas. Mention of 'imposex' and discussions thereon are scattered throughout the book, leading to something of a multiple coverage of this aspect. This is a small criticism, however, of a very useful work which I am very happy to recommend. It is very good value at £50.

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### **Organic Reactions, Vol. 50: The Stille Reaction**

V. Farina, V. Krishnamurthy and W. J. Scott

John Wiley, New York, 1997

xx + 676 pages. £70

ISBN 0-471-15657-4

This Golden Anniversary volume of *Organic Reactions* is devoted entirely to a review of the Stille reaction. This reaction, which was developed by J. K. Stille in 1978, involves the reaction of an organotin(IV) compound  $R^1SnR^2_3$  and a compound  $R^3X$  in the presence of a palladium(0) catalyst,  $Pd(0)L_m$ , to give the carbon-carbon-coupled product  $R^1-R^3$ .  $R^1$  is typically a vinyl, aryl, alkynyl, allyl or alkyl group,  $R^3$  is usually vinyl, aryl, allyl, benzyl or acyl, and X is a halide or sulphonate.

Similar reactions of the organic compounds of magnesium, zinc, boron and silicon are known, but the stannanes show a convenient balance of stability and reactivity: their use has been widely developed and exploited in recent years, and the Stille reaction has been used with spectacular success in the final or late stages of synthesis of some natural products. The reaction was reviewed by J. K. Stille in 1986 and by T. N. Mitchell in 1992, and recent advances were described by V. Farina and G. P. Roth in 1997, but a comprehensive and authoritative review has been urgently needed before the subject grows to an unmanageable size.

Following the established pattern of *Organic Reactions*, the volume starts with a rather brief discussion of

the mechanism, regiochemistry and stereochemistry of the reaction, and of its scope and limitations. The stannane reactants are usually stable to air and moisture, and are unreactive towards most types of functional groups which may be present in  $R^3X$ , and which therefore do not need protecting. When the reactivity of the stannane is low (e.g. when  $R^1$  is alkyl), the reactivity can be enhanced by working with a polar aprotic solvent such as DMF, DMSO or HMPA, and a weak ligand L, such as triphenylarsine or tri(2-furyl)phosphine, rather than triphenylphosphine. If the reactions are run under an atmosphere of carbon monoxide, a carbonyl group can be incorporated into the product  $R^1COR^3$ ; further modifications of the process involve organostannanes where  $R^1$  is H,  $R_3Sn$ , RO or  $R_2N$ . This introductory section of 60 pages ends with a discussion of the experimental conditions and nine examples of typical preparations.

The rest of the book is occupied by a series of tables, classified mainly on the basis of the nature of the group  $R^3$  in the electrophile  $R^3X$ . The substrate, stannane, conditions, yield and reference are given, and the literature is covered up to the end of 1994, with some selected references from 1995. These tables occupy 560 pages and include some 5000 examples of the reaction. There are 865 references.

This is a worthy anniversary volume in this renowned series, and will be a valuable source of information for all synthetic organic chemists.

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### **Theoretical Aspects and Computer Modelling of the Molecular Solid State**

Angelo Gavezzotti (ed)

John Wiley and Sons, Chichester, 1997

237 pages, £70

ISBN 0-471-96187-6

Molecular solids are those solids where the forces between neighbouring particles are much weaker than the forces within the particle. Solid phases of neutral organics and organometallics are molecular; ionic, covalent and metallic solids are not. In this book, Volume 1 in the series *The Molecular Solid State*, the structures and morphologies of molecular solids and their thermodynamic properties and phase transitions are described and explained in terms of the intermolecular forces which keep the molecules together. It is a welcome and timely addition to the scientific literature in the rapidly developing field of computer simulation of intermolecular interactions. It comprises seven chapters, each written by an expert or experts. In his foreword J. D. Dunitz, the Series editor, points out that the weak intermolecular interactions, which include hydrogen bonding, are responsible for the existence of the organic world; that the long-range periodic order of a crystal is a

consequence of the short-range interactions between neighbouring molecules; and that with the developing interest in intermolecular interactions the focus of interest in crystallography is shifting from an emphasis on molecular structure towards the systematics of intermolecular interactions. Although we can now simulate the crystal structures of a number of compounds we are still far from being able to predict crystal structures in general. The aim of this book, admirably achieved, is to review progress and point the way ahead.

The dominant intermolecular forces which enable the ordering of molecules in a crystal are the van der Waals attraction, hydrogen bonding and electrostatic interactions. The lattice energy of a crystal having  $N$  molecules, each with  $n$  atoms, surrounding a molecule of  $m$  atoms is simply

$$E_{\text{cr}} = 1/2 \sum_{k=1}^N \sum_{i=1}^n \sum_{j=1}^m V_{kij}$$

where  $V_{kij}$  is the interaction energy between atom  $i$  of the central molecule and atom  $j$  in the  $k$ th surrounding molecule. The interaction energies are evaluated as functions of interatomic distances by, for example, the Lennard-Jones potential or the Buckingham potential with coulombic potentials and hydrogen-bond potentials as required. The stable, lowest-energy, structure and its evolution with temperature, pressure and time are commonly sought by a molecular dynamics simulation—wherein lie the skills required and the pitfalls for the unwary.

In Chapter 1, A. Gavezzotti provides a masterly account of crystal symmetry and molecular recognition. The space groups are built from combinations of the symmetry elements of a molecule (translation, inversion centre, glide plane, twofold screw axis). The text is accompanied by exceptionally well-drawn diagrams; a computer program for the construction of space groups is cited. The chapter includes useful discussions of fivefold symmetry (and misconceptions relating thereto), problems with X-ray-derived crystal symmetries (symmetry violations due to small atomic displacements, structural disorder at the molecular level), chirality, thermodynamics of crystal growth and dissolution, space filling and crystal design. The chapter concludes with a useful descriptive list of leading references. Subsequent chapters fill in and expand on the themes of the first chapter, giving the book a unity often lacking in multi-author works.

S. L. Price in Chapter 2 tackles the theory of intermolecular forces, how intermolecular potentials are derived and how they are applied to account for and predict crystal structures with particular emphasis on the electrostatic and polarization contributions to the intermolecular potentials of polar molecules (the distributed multipole model). The point is well made that close-packing 'knobbly' molecules may form tightly bound three-dimensional jigsaws whereas planar or disc-shaped

molecules can be close-packed in a range of structures and so able to slide and rotate relative to each other.

In Chapter 3 A. Gavezzotti and G. Filippini describe the calculation of thermodynamic quantities (lattice vibrations, enthalpy, entropy and free energy of sublimation, vapour pressure and specific heat, enthalpy of melting, heats of mixing) from atom-atom potentials. Solvates and inclusion compounds are discussed from the standpoint of host-guest chemistry, the guest behaving as a space filler in crystallization. Packing energies are compared with experimental heats of sublimation. A useful table of atom-atom potential parameters is provided.

Energy minimization by force-field methods (molecular mechanics and dynamics, Monte Carlo) is described in Chapter 4 by B. P. van Eijck, L. M. J. Kroon-Batenburg and J. Kroon. Concepts are defined clearly and carefully with the relevant mathematics. Various force fields and their parameterization are described. Applications are to crystal structure calculations, modelling carbohydrates and cellulose in particular, and defining hydrogen atom positions and disorder (not always accessible by X-ray crystallography). This chapter is a most useful summary of the equations and methods of force-field calculations, with timely warnings of the pitfalls.

In Chapter 5 L. S. Bartell discusses experimental studies and molecular dynamics simulations of homogeneous nucleation in molecular clusters, especially spontaneous phase changes when a system is cooled. Although many nucleation processes are heterogeneous, initiated intentionally or inadvertently by seeding, an understanding of homogeneous nucleation is a requisite for developing heterogeneous models. Homogeneous nucleation is studied experimentally by electron diffraction and high-resolution coherent Raman spectroscopy of supersonic jets, and theoretically by MD simulations and visualizations of phase transitions. Results for alkyl halides,  $\text{TeF}_6$  and  $\text{SeF}_6$  are reported. The simulated phase changes closely parallel those observed in supersonic jets.

The final two chapters are devoted to crystal structure and morphology. In Chapter 6 R. J. Gdanitz reports a number of successful ab-initio molecular dynamics predictions of crystal structures. In Chapter 7 G. Clydesdale, K. J. Roberts and E. M. Walker review experimental data on crystal habit and progress in predicting crystal morphology, including the effect of modifying additives and the use of the computer program HABIT95.

This is a wide-ranging book which will be useful both to the novice and the expert in computer simulations and to black-box practitioners of the modelling art. I enjoyed reading it and learned a lot from it. I strongly recommend this book to anyone who wishes to understand how and why molecules pack into crystals and to learn more about

the computational and experimental techniques used in studying molecular interactions.

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**Advanced Practical Inorganic and Metalorganic Chemistry**

R. J. Errington

Blackie Academic and Professional, 1997

xii + 288 pages. Soft cover £24.99

ISBN 0-7514-0225-7

This eminently readable book has been written to bridge the cultural gap for students moving from carrying out synthetic chemistry in a teaching environment to performing preparative chemistry in a research environment. The emphasis is on the handling of air-sensitive compounds, although methods for the characterization of compounds are covered briefly in later chapters.

Important preliminaries for the new research student, such as searching and keeping up to date with the chemical literature, and the maintenance and content of laboratory notebooks, are prominently featured in the introductory chapter.

The use of Schlenk lines, glove boxes and high-vacuum lines is comprehensively covered. For example, in the chapter devoted to Schlenk techniques we are taken through a discussion of aspects of the design and setting up of an inert-gas/vacuum manifold, to considerations of the inert-gas supply and purification columns, and finally to a description of filtration techniques using Schlenk apparatus.

Having considered the apparatus to be used in our experiments the author then moves on to discuss the solvents and reagents which might be employed. There is much useful information collected here on the purification and drying of solvents (including the design and maintenance of solvent stills). The section on reagents is by its very nature somewhat general. Nevertheless the author provides a host of useful ideas for carrying out halogenation, ligand metathesis, alkylation, oxidation, reduction and deprotonation reactions.

By this stage we are ready to carry out a reaction! Focusing on air-sensitive materials, the author discusses techniques for the measurement of quantities of reagent and their introduction to the reaction vessel, and for heating and mixing the reaction mixture. Subsequently of course the products must be worked up, isolated and purified and the ways in which this can be achieved are quite thoroughly described. There is also a useful discussion at this point of the long-term storage of sensitive materials in ampoules. The growing importance of the reactions of solids is recognized by the author and discussed here in two short chapters.

Characterization of products now follows, the emphasis being on the preparation of samples for measurement,

rather than the theory of particular techniques, as is appropriate to the general thrust of the text.

Special techniques such as microwave heating, metal vapour synthesis and sonication are treated briefly in the penultimate chapter and the book concludes with short descriptions of preparative methods for selected compounds, which largely reflect the author's own research interests.

In conclusion, the text is lucid and is supplemented by many clear line drawings of apparatus. The book will be of interest to anyone embarking on a career in preparative chemistry and should also provide more experienced researchers with new ideas on how to carry out their synthetic studies.

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**Edward Frankland: Chemistry, Controversy and Conspiracy in Victorian England**

C. A. Russell

Cambridge University Press, Cambridge, 1996

xx + 535 pages. £65.00, 110.00

ISBN 0-521-49636-5

All cultures need their heroes, and organometallic chemistry has an excellent one in Edward Frankland. In the past he has been undersung but, with this scholarly researched and referenced biography by Colin Russell, Frankland should now receive the recognition he deserves.

He was born in Churchtown, near Lancaster, in 1825, the illegitimate son of Edward Gorst Jr and Margaret Frankland, who was a servant in the home of Edward Gorst Sr, a prominent lawyer in Preston. Soon afterwards, his mother married William Helm, and Frankland lived in Lancaster with his stepfather and mother, who took in lodgers for a living. He never gave interviews, and though his own recollections were published in 1901 as *Sketches from the Life of Sir Edward Frankland*, this was rapidly withdrawn before reappearing in an expurgated edition. The secret of his origins was suppressed, and this may have influenced the fact that neither the Royal Society nor the Chemical Society published an obituary when he died in 1899.

Colin Russell and his wife Shirley very fortunately came across a collection of several thousand documents in the hands of Frankland's descendants. Microfilm copies of these papers have been deposited in the Open University Library, and it is largely on these papers that the present book is based.

After a rudimentary education at eight different schools, Frankland was apprenticed for six years to a pharmacist's shop in Lancaster; then in 1845, on recommendation of a medical friend, he moved to London to be assistant in analytical chemistry to Lyon Playfair of the Geological Survey. Here he met Kolbe, who was to be a life-long friend. He attended Playfair's