

# PREPARATIVE CHEMISTRY USING SUPPORTED REAGENTS

*Edited by*

**PIERRE LASZLO**

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## PREFACE

I know a wonderful little inn on a hillside, in the eastern part of France. It sports on its facade a feature out of a painting by Magritte: glass doors with deer antlers as handles. Reflections in these are of white clouds, plus the dark blue of the mountains, wavelet after wavelet, merging into the light blue of the sky.

In like manner, the subject matter of this book is practical, eerie, harmonious. It tells of a new dimension in the methodology of organic reactions. Adsorption of reactants and of reagents on solid supports upgrades the processes into efficiency, selectivity, and trivially easy work up.

The reasons for such routinely achieved successes are still somewhat mysterious—indeed this volume could quite profitably be used as a source book in surface science. This is also why quite a few chapters have been included on the physical methods for study and characterizing surfaces and their adsorbates, and on chemical reactivity at interfaces.

The eeriness has also to do with the harmony: that chapters on apparently distant topics such as polymer-supported reagents, shape-selectivity within zeolithes (spelled, less correctly but more according to tradition, zeolites in the rest of the book), and graphite intercalates could nevertheless fall into place like stained glass of various colors in a church window.

Medieval windows and, say, the *Wall Street Journal* have one thing in common—they make concise statements about complex matters. Each chapter here tells a different story, but one stripped to the essentials.

The whole is a rather comprehensive description (within the limited format allowed by the publishers) of a budding new field of chemistry, as well as a compendium of useful new techniques. The entire range, from the essential theoretical concepts to the "how to" technical aspects, is here.

One further word about this book is organization: I have cast the net wide, because this is a new field, the limits of which, at present, are beyond the horizon.

My fellow authors could have been drawn from Rembrandt's "Anatomy Lesson": skilled experts, intent on doing a highly professional job. Many



are world-famous scientists, very much esteemed and very much in the public eye. They have all accepted their assignments with grace and with gusto. That they have all treated my editorial emendations and cuts with benign tolerance is further proof that they are gentlemen and scholars.

Some of this book was prepared while I benefited from visiting professorships, which gave me the calm, the library browsing, and the outdoors backpacking—all mandatory ingredients for this individual. I am grateful to the University of Hamburg (Professor Armin de Meijere), to the Institute of Molecular Science, in Okazaki, Japan (Professor Iwamura Hiizu), and to Cornell University (Professor Roald Hoffmann) for these generous invitations.

Finally, I have heeded the call of clean and delicate graphics. While the in-house staff at Academic Press have been up to their usual high standards, I am indebted for the cover design to Valerie Annette Seelig, of WFW Productions. I take this opportunity to thank warmly my co-worker of many years, Madame Lucienne Souka, for typing the index on very short notice.

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## Part I

# **Supported Reagents: General Principles**





# 1 HOMOGENEOUS AND HETEROGENEOUS REACTION CONDITIONS\*

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and  
Ecole Polytechnique  
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## I. THE ALCHEMICAL HERITAGE

The distinction goes back to the alchemists and, beyond them, is traceable to Chinese categories of thought, which have thus fertilized Western science. Chemical transformations can be made to occur according to either the wet way or the dry way. The wet way comes close to what continues to be known in today's laboratories as wet chemistry, i.e., solution chemistry. The dry way was chosen by the alchemists for processes such as tincture of metals. It was effected typically by heating a mix of various substances as solid powders.

In modern times, and in most preparations of fine chemicals, whether in academic or in industrial laboratories, the wet way is dominant. It has become the highway chemists travel along. The dry way, if not totally abandoned, has become a byway, at least for such preparations. Yet, as

\* Research on preparative chemistry using supported reagents in my laboratory was made possible by a grant from Programmation de la Politique Scientifique, Brussels (Action Concertée 82/87-34).

this book will document, it is one of the multiple origins for preparative chemistry using supported reagents.

Our alchemist ancestors bequeathed to us another handling procedure for chemicals which, besides being basic to our science, is also another distant relative of modern supported preparative chemistry. Filtering is perhaps the most elementary act in separation science, hence its practical importance for chemistry. Filtering is also pregnant with the whole of chromatography.

There is yet another lesson from history. Think of it for a minute, and you might share my initial bewilderment (which led to my entering this field). We still run chemical reactions in much the same way as in the seventeenth and eighteenth centuries. In our age of sophisticated electronic instrumentation, sensors, microprocessors, and robots starting to see use in chemical synthesis, reaction flasks stand on our benches like relics from a distant past.

The reason is that they embody premodern concepts (dating back to the last quarter of the eighteenth century) about the virtue of dissolution, the attendant freeing from one another of the particles of matter. This is one of the most primitive and one of the most general means of activating chemicals: by dissolving a solid, we remove the attractive intermolecular forces present in the crystalline lattice. Since many dissolutions are often exothermic, these forces are not fully compensated by the resulting solvation forces. Such an idea was, one might say, both the dominant paradigm and the trademark of the chemists of yesteryear.

Very often textbooks of the time stressed this concept. I shall take as my example a book from 1803, embodying the chemical concepts taught at the young Ecole Polytechnique in Paris (founded in October 1794) by leading French chemists such as Berthollet, Fourcroy, Chaptal, and Guyton de Morveau. The author, Ségur, starts his book with the laws of chemical attraction. The first law is that attraction, leading to chemical combination, can only be present between the ultimate particles of matter. The second law states that this combinational attraction must destroy the aggregation forces between molecules. The third law states accordingly that for two chemicals to be submitted to combinational attraction at least one must be a fluid. Ségur writes that the "phenomenon of dissolution is due to this law." He makes this astute and perceptive comment (in my free translation): "the expressions of 'solvent' and 'solute' are improper. These terms seem to imply that one of the bodies is passive, while the other one, the *fluid*, is the only one to be active, the only one whose influence determines the change of state. The truth of the matter however is that the solid tends as much to solidify the liquid, as the liquid tends to liquefy the solid" (Ségur, 1803).