Section I

Section I, comprising Chapter 1, is the shortest of the five sections in this monograph on the chemical biology of carbon. The operating premise is that carbon chemical biology is nothing more or less than the organic chemistry of life. To that end Chapter 1 starts with the persistent tetravalency of carbon and the proposal that the inventory of tens of thousands of organic molecules (metabolites) can be parsed into a limited set of functional groups and straightforward chemical routes for their interconversion.

The four key general categories of functional groups for *in vivo* chemistry are alkenes (olefins), C–O, C–S, and C–N functional groups. Within the C–O, C–S, and C–N groups many are interconnected by two electron redox steps. A second general tenet of this book is that carbacycles and heterocycles (oxygen-, nitrogen-, and sulfur-heterocycles), their formation, reactivity, and accessible chemistry, are key determinants that enable much of the primary metabolic functional group transformations.

For the predominant two electron reaction pathways for metabolite interconversions, the concept of carbon nucleophiles as electron rich species that attack electron poor electrophilic carbons puts a logical framework on *in vivo* organic chemistry.

These above three convergent approaches to the kinds of organic functional groups available in carbon chemical biology set the stage for a third major precept: that there are only four reaction types that make or break C–H and C–C bonds in both abiotic and biotic organic chemistry. These are carbanion-driven reactions, carbocation-driven reactions, carbon-radical driven-reactions and pericyclic reactions (concerted *via* cyclic transition states).

Our approach to carbon chemical biology is then fourfold: (1) available carbon-based functional groups; (2) the most common carabacyles and heterocycles (including 10 of 13 human vitamins); (3) nucleophilic carbons attack electrophilic carbons to make new C–C bonds; and (4) there are few mechanistic routes to make and break C–H and C–C bonds. These four reactivity parameters explicitly encompass the underlying logic of metabolic pathways that constitute the organic chemistry of life.