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Book review

Ion-radicals in organic synthesis, by Z.V. Todres, Khimia Publishers, Moscow, 1987, 240 pages, 2.80 roubles

Modern organic and organometallic chemistry is much concerned with investigations of the structure and reactivity of labile intermediates involved in the pathway from the initial substrate to the end product. Such studies allow better understanding of the reaction mechanism, and so lead to new ideas for increasing the reaction rate and improving the yields of the final products. Until recently, attention has mainly been focused on radicals or charged species, i.e., carbanions and carbo-cations (carbenium ions). The species of intermediate nature, ion-radicals, which show both ionic and radical properties, were for a long time beyond the scope of direct study. However, much more is now possible because of the development of more refined instruments and much attention has recently been given to phenomena that were little studied or even completely unknown in earlier decades.

This monograph by Todres summarizes researches on the structure and reactivity of organic ion-radicals. The application of ion-radical reaction in organic synthesis receives special attention. With the abstraction or addition of one electron an organic molecule is transformed into the ion-radical state, the energy of the system thereby being increased, but this energy change is usually not very large and considerably lower than that required for photo-induced activation. In recent years the moderate energetic influences which cause changes of organic molecules during liquid-phase electron transfer have been discussed, and much attention has been given to the electron transfer stage in homogenous reactions which were previously regarded as purely ionic or purely radical in nature. This matter is of both theoretical and practical importance. A new field of organic and organometallic chemistry, that of reactions of the ion-radical type has been discovered, and knowledge of the principles of these processes can provide a stimulus to the development of organic synthesis.

This book presents an account of ion-radical reactions and tries to set out their synthetic possibilities as fully as possible, while at the same time retaining its integrity and avoiding minor details (as is essential in view of its small size). The breadth and importance of the problem certainly merits both an in-depth analysis, and a wide coverage, but a multi-volume contribution would be of interest only to narrow specialists and a popular-superficial coverage would not attract the attention of the serious reader.

The author sets out to systematize the material available, mainly on the basis of recent information. This approach is undoubtedly of help for specialists, since it makes it possible to comprehend the subject as a whole and to see the possibilities of new applications and concepts. The book should appeal to a wide range of chemists, since it is based on the comparison of the properties of ion-radicals and of

organic molecules that generate ion-radicals. This makes the book of special interest to organometallic chemists, especially since it is by a recognized specialist working at the well-known A.N. Nesmeyanov Institute of Elementoorganic Compounds, Academy of Sciences of the U.S.S.R., and it should contribute greatly to the development of new applications in organometallic chemistry.

The book consists of six chapters. Chapter 1 deals with the special electronic structure and reactivity of organic ion-radicals. Chapter 2 presents an analysis of the methods for preparing ion-radicals, and discusses the electron-equilibrium and some specific features of liquid phase redox processes. Chapters 3 and 4 are concerned with the ion-radical nature of various organic reactions and pay special attention to the methods of detecting reactions of this type. Chapter 5 is concerned with the less famous but promising field of ion-radical stereochemistry. Chapter 6 summarizes the important synthetic methods based on ion-radical processes. The examples presented show that the ion-radical approach to synthesis has significant advantages, and the products obtained can be of much practical value. The prospects for the development of organic ion-radical chemistry are discussed in the final chapter. A careful analysis is made of the outstanding problems and the achievements to date, and the possibilities of the development of the organic chemistry of ion-radicals are outlined.

Novel interpretations and convincing arguments hold the reader's attention. Advances in the field of organic ion-radical chemistry will surely have much influence on the development of organometallic ion-radical chemistry. The International Conference on Electron Transfer held in Sweden in 1987 singled out for a special discussion, the topic "Rôle of Electron Transfer in Organometallic Chemistry; a Sleeping Giant?" and this book will help organometallic chemists see the potential of organometallic ion-radical chemistry.

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