

Preface

It is almost impossible to explain how a scientist who is engaged in the basic science creates his field of research. This personal process cannot be comprised within any of the formal concepts of philosophy of science. It could just appear that, during the work, an extra observation discovers a new phenomenon so interesting and intriguing that it directs the researcher to investigate in quite a different course.

My previous scientific interest in the structure and vibrational spectroscopy of carbocations in solid state was developed in such a direction, that the next step must include also a study of other organic cations, which could appear as reactive intermediates in organic reactions. The first candidate was the nitrenium cation, an extremely elusive molecular species. The task was difficult, but it is known that doing the serious science means a selection of difficult problems to deal with. On the way to the isolation of nitrenium cations, the study of appropriate precursors was necessary. One of them is nitrosylchloride, which is a reactive molecule that easily adds to the carbon-carbon double bond forming the alpha-chloro nitroso compounds. Since our approach has been based on the reactions of intermediates in the solid state, one of the molecules interesting for study was 3-chloro-2-nitrosonorbornane. Following the standard procedure in the solid-state chemistry, it happened that we had irradiated the crystals of such a norbornane derivative by UV light under the cryogenic conditions. Surprisingly, the crystals changed color from yellowish to deep blue. By warming the sample the color disappeared. Successive change in color induced by irradiation and warming could be repeated several times. Discovery of this photochromic-thermochromic effect in the solid-state seemed so interesting that it had redirected our research program to the new field of nitroso compounds. The observed photodissociation of nitroso dimers to monomers and their redimerization in crystals or in polycrystalline environments seemed to us as an opportunity to use these molecules as models by which basic solid-state reaction mechanisms could be studied. Such a way our new research field was opened. Later, after the experience in nitroso chemistry, aromatic derivatives emerged as especially interesting because their chemistry can serve as modeling system not only for the solid-state reactions, but also for a series of the chemical phenomena and concepts.

After publication of our basic works, I had the honor to receive a letter from Prof. Brian G. Gowenlock, who is a nestor in the chemistry of nitroso compounds, and who has inspired me to continue in investigating these fascinating molecules. Our correspondence was for me a strong intellectual impulse for continuing our study in this direction, and I take here the opportunity to thank Prof. Gowenlock for his suggestions, support and inspiration.

This book is also a result of the idea to prepare a manuscript about my research, which I have received from the Editor, Springer-Verlag. After some period of consultations I accepted to write the book about the chemistry of C-nitroso compounds with the intention to comprise not only our recent work, but also the wider aspects, such as spectroscopy, typical reactions, or reactions of biological interest.

The work in this form is the result of all of my collaborators in the research group, as well as of my colleagues who, by their suggestions and comments, noticeably improved the manuscript. I thank Prof. Zlatko Mihalić, Prof. Srđanka Tomić-Pisarović, Dr. Ivana Biljan, Dr. Srđan Milovac, Ms. Katarina Varga, my students Ana Maganjić and Ivan Šolić, and especially librarians Branka Maravić and Zdenka Kuri. The research that was the base for a great part of this work has been financially supported by the Ministry of Science, Education and Sports of the Republic of Croatia (Grant 119-1191342-1334). The support is gratefully acknowledged.

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