

BOOK REVIEW

Substituent Effects in Radical Chemistry

NATO Advanced Science Institute Series C: Mathematical and Physical Sciences 189, Eds. Heinz G. Viehe, Zdenek Janousek and Robert Merényi, D. Reidel Publishing Company, Kluwer Academic Publishers Group, Dordrecht, Boston, Lancaster, Tokyo 1986, xiv + 482 pp. Price: Dfl. 195,00 / US \$ 79.50 / £ 58.25

The handy book of half a thousand pages is actually the Proceedings of the Conference on Substituent Effects in Radical Chemistry, held in Louvain-la-Neuve (Belgium) January 20-24, 1986.

The meeting among a number of leading experts (almost 50 specialists) led to the 40 lectures and posters presented in this book.

The Preface written by the editors of the book states: "Respectably old radical chemistry which plays a major role in life-processes, both desired (e.g. breathing) and non-desired (e.g. inflammatory diseases, ageing) has been gaining new youth in the past decade".

Indeed, during the last decade organic free-radical chemistry has undergone a remarkable metamorphosis from an area of limited utility for the construction of carbon-carbon bonds, except in polymers, to one of major synthetic importance with methods capable of providing chemo-, regio- and stereo-selectivity far beyond the most optimistic expectations of early workers in the field.

The topic chosen seems to be essential for the whole radical chemistry: understanding and exploiting (single and multiple) substituent effects on radicals.

Up-to-date spectroscopy and other physical methods, recent advances in computational techniques as well as mechanistically well understood syntheses led to a number of interesting developments in the field of radical chemistry. The results of these achievements will reach beyond the field of organic chemistry

into biochemistry, biology and even medicine.

"New reactions useful in synthesis are usually discovered by accident. It is, however, possible to invent reactions by conception" said D. Barton in his lecture. To design new radical chain reactions useful in synthesis, it is necessary to know and use disciplinary radicals - whatever the cause of their constructive behavior. This is exemplified by the paper of Barton et al.

The captodative (cd) stabilization - in fact a rediscovery and an actualisation of "merostabilisation" or push-pull-interaction (Dewar, Katritzky, Balaban) - proved to be an excellent concept in the papers of Viehe et al. to create selective free-radical addition or abstraction reactions. The authors proposed an explanation of the phenomenon by the change of polarization when a radical is formed, and called it as Radical Umpolung.

The cd-radicals would generally prefer to dimerize and the dicaptor ones to undergo other reactions due to the destabilization of their dimer. Particularly in the presence of an olefin, dicaptor species would prefer the chain addition to the dimerization reaction. On the other hand, didonor radicals would always be obtained at lower rates than the other species but if they are formed, nothing but steric effects would hinder their dimerization.

The cd substitution leads to selectivity, not previsible considering polar effects only. For example, in neat phase the methyl methoxyacetate gives selectively by oxidation, even in competition with dicapto or didative analogs, the symmetrical captodative dimer. Radicophilic olefins with 1,1-cd-substitution are used as efficient radical traps: again, nearly exclusive symmetrical dimerization is observed by capturing all kinds of radicals by these captodative olefins (R. Merényi, H.G. Viehe et al.). Thus, the factors determining rates and selectivities for radical addition to double bonds, or for H-abstraction are now well clarified.

"Synthetic applications of the polar effects of the substituents in free-radical reactions" (F. Minisci) and "Non-chain radicaloid mechanism of some nucleophilic substitution reac-

tions" (A.R. Katritzky) are two papers that constitute the overlap area between radical and ionic chemistry.

"Captodative substituent effects in cycloaddition reactions" (L. Stella), "1,3-Dipolar cycloadditions" (D. Döpp), "Photo Diels-Alder addition of cd-alkenes" illustrate the novel applications of the controlled radical processes.

The growing interest in the fundamentals of free radical properties and behavior, is reflected by a number of papers showing the continuing importance of ESR in determinations of and measurements on free radicals (D.R. Arnold, K.U. Ingold, R. Sustmann, H. Fischer, B. Giese).

Gradually moving from findings of experimentalists to the results of theoreticians inter alia, G. Leroy (A theoretical approach to substituent effects in radical chemistry), P.R. Schleyer (The contrasting strain energies of small rings), D. Kost (ab-initio calculation), J. Fossy (PMO approach), B. Giese et al. (Orbital effects in carbohydrate radicals) are to be mentioned.

Whereas many questions remained open concerning the extent and the additivity of the radical stabilizing effect of substituents, several synthetic and physico-chemical results support the novel concepts today.

Beyond the acceptance (or nonacceptance) of cd-effect there are discussed some other polemic questions; e.g.: in Schleyer's opinion there appears to be no need to invoke "sigma aromaticity" (proposed by Dewar recently, 1985) to explain the stability of cyclopropane. D. Döpp et al. have shown that 1,3-dipolar cycloaddition of an E- and Z-pair of captodative alkenes did occur stereospecifically in accordance with Huisgen's concerted mechanism (1976), and in contrast to Firestone's view (1977) of a spin-paired diradical intermediate.

Beside the usual Table of Contents, a carefully compiled subject index (12 pages) is attached to the volume to help its use. The current state of intense activity in the field of

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radical chemistry is reflected by the fact that more than 90 % of the almost 700 (!) papers cited in the book have been published during the last decade.

This book as a top level scientific kaleidoscope is recommended to all organic chemists and related researchers who wish to know and apply the results of the modern radical chemistry. Anyone who would like to participate in the exciting further development of this area should read this book from cover to cover.

A. Messmer

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Photophysical and Photochemical Tools in Polymer Science

NATO Advanced Science Institute, Series C: Mathematical and Physical Sciences, Vol. 182. Ed. Mitchell A. Winnik. D. Reidel Publishing Co., Kluwer Academic Publishers Group, Dordrecht, Boston, Lancaster, Tokyo 1986, xi + 642 pp. Price: Dfl. 260.00 / US \$ 124.00 / £ 82.50

The volume comprises the amended texts of 27 lectures of "Advanced Study Institute" organized with the same title at San Miniato, Italy, in October 1985. According to the definition of the Editors "An Advanced Study Institute should be organized as a school, with the teaching function taking precedence over the announcement of new research findings". Accordingly, the majority of the papers expounds the theoretical and experimental basis of method(s) applied, over and above that, however, most authors take the opportunity of reporting the newest (mainly their own) results. Thus, the volume leads the reader from the fundamental principles to the up-to-date results, to the present front line of research.

The volume is introduced by the comprehensive lecture of H. Morawetz under the title "Fluorescence Phenomena Useful for the Study of Polymers", in which the author systematically

explains the basic principle of fluorescence polarization. He treats the effect of microenvironment and the process of quenching and excimer fluorescence.

The further lectures are grouped by the Editor into four chapters. In the first chapter six lectures can be found under the title "Spectroscopic Methods". The lecture of S. Tazuke and M.A. Winnik provides a general introduction to the techniques of fluorescence and phosphorescence spectroscopy. The discussion of common artifacts is of special interest. In the first presentation of H. Masuhara the transient absorption spectral measurements in the ns and ps time range are described. Various artifacts (some nonlinear factors) have to be examined in order to obtain accurate absorption spectra. In his second lecture, he shows that the electron transfer processes lead in polymers to exciplexes or ion radicals. Studies of polymers carrying medium-sensitive fluorophores (dansyl groups) show that a part of the conformational transition is slow enough to be followed by stopped-flow technique (H. Morawetz). I. Soutar and D. Phillips review the intramolecular excimer formation and the results obtained from the time dependence of fluorescence in synthetic polymers.

The chapter "Polymer Solutions and Melts" contains 10 publications. In the paper of E. Helfand some of the fundamental polymer theory underlying many phenomena (equilibrium properties of dilute and semi-dilute solutions, relaxation of single and entangled macromolecules, dynamics of conformational transitions) are reviewed. For local molecular dynamics studies of polymer chains, proper fluorescence of chromophores covalently linked to a chain unit (J. Vandendriessche et al.) or built into the main chain (L. Monnerie and J.-L. Viovy) was used. Results obtained by fluorescence polarization on anthracene labelled polystyrene stretched at various temperatures and strain rates are discussed. The spectroscopic studies of rates of hindered rotation if one energy barrier is surmounted in conformational transitions of polymer backbone (H. Morawetz). Using a laser flash photolysis, the dynamics of the conformational change has been followed in the  $\mu$ s range (M. Irie). The paper of M.A. Winnik

provides a review of recent theoretical concepts and a description of experiments based upon luminescence spectroscopy, which allow one to investigate the cyclization of macromolecules in solution.

The organizers made a decision not to distinguish between synthetic and biological macromolecules, since, using the same techniques, one can extract similar information about their respective systems. Accordingly, two papers have been included in the collection: "Folding and Dynamics of Proteins Studied by Non-Radiative Energy Transfer Measurements" by E. Haas and "Rotational Dynamics of Biological Macromolecules" by E. Blatt and T.M. Jovin. The chapter is closed by the study of B.A. Smith which deals with methods used to measure the tracer diffusion coefficient of polymer molecules which have been labeled with photochromic or fluorescent dyes.

The chapter "Polymers in the Glassy State" consists of five publications. The paper of J.J. Aklonis deals with the current problems in understanding the behavior of polymer glasses (the thermodynamic theory and the kinetic or ordering parameter models). A series of fluorescence probes, "molecular rotors" has been developed by R.O. Loutfy. The internal rotation of these compounds can be slowed down by increasing the surrounding media rigidity or decreasing the free - volume available for molecular relaxation. The glass-rubber transition was studied by L. Bokobza and L. Monnerie, using fluorescence probe. Luminescence measurements can be used both to detect transitions, at which particular modes of molecular motion become observable, as well as providing sensitive methods for measuring diffusion and permeability in solid polymers (J.E. Guillet). In the last paper of this chapter recent theoretical studies on electronic excitation transport among chromophores attached to a polymer chain are reviewed (C.W. Frank et al.).

The closing chapter "Polymer Blends and Phase Separation" contains five papers as well. This chapter is devoted to publications dealing with the investigation of the properties of bulk polymers, rather than those of individual macromolecules.

C.W. Frank et al. demonstrated that excimer fluorescence is sensitive to changes in a number of parameters that are expected to affect the Gibbs free energy of mixing. Emission spectra of polymer blends tagged with fluorescent labels can be used to characterize polymer compatibility (H. Morawetz). The objective of the paper of C.W. Frank and E. Gelles is the photophysical analysis of the fluorescence in terms of the morphology of the polymer blend. The phenomenon of static quenching of the fluorescence emission of anthracene-labeled polystyrene is used for the analysis of phase separation by J.L. Halary and L. Monnerie. According to M.A. Winnik, from the rates and efficiency of quenching, one can learn about local morphology, the extent of interphase formation and the molecular relaxation processes in individual phases of the material.

The volume is essential to researchers and institutions working in this well reviewed, broad field of science. The prompt issue of the volume has been made possible by the photoprint technique, by the direct use of very carefully prepared manuscripts.

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