Substituent Effects in Radical Chemistry

NATO ASI Series

Advanced Science Institutes Series

A series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation
B Physics	London and New York
C Mathematical and Physical Sciences	D. Reidel Publishing Company Dordrecht, Boston, Lancaster and Tokyo
D Behavioural and Social Sciences	Martinus Nijhoff Publishers
E Engineering and Materials Sciences	The Hague, Boston and Lancaster
F Computer and Systems Sciences	Springer-Verlag
G Ecological Sciences	Berlin, Heidelberg, New York and Tokyo

Substituent Effects in Radical Chemistry

edited by

Heinz G. Viehe

Zdenek Janousek

and

Robert Merényi

University of Louvain,
Louvain-la-Neuve, Belgium

D. Reidel Publishing Company

Dordrecht / Boston / Lancaster / Tokyo

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Research Workshop on
Substituent Effects in Radical Chemistry
Louvain-la-Neuve, Belgium
January 20-24, 1986

Library of Congress Cataloging in Publication Data

Substituent effects in radical chemistry.

(NATO ASI series. Series C, Mathematical and physical sciences; vol. 189)
Proceedings of the NATO Advanced Research Workshop on Substituent Effects in
Radical Chemistry, Louvain-la-Neuve, Belgium, January 20-24, 1986.

"Published in cooperation with NATO Scientific Affairs Division."

Includes index.

1. Radicals (Chemistry)—Congresses. I. Viehe, Heinz Günter. II.
Janousek, Zdenek. III. Merényi, Robert. IV. NATO Advanced Research Workshop
on Substituent Effects in Radical Chemistry (1986 : Louvain-la-Neuve, Belgium) V.
Series: NATO ASI series. Series C, Mathematical and physical sciences; vol. 189.
QD471.S86 1986 541.2'24 86-17895

ISBN-13: 978-94-010-8614-1 e-ISBN-13: 978-94-009-4758-0

DOI: 10.1007/978-94-009-4758-0

Published by D. Reidel Publishing Company
P.O. Box 17, 3300 AA Dordrecht, Holland

Sold and distributed in the U.S.A. and Canada
by Kluwer Academic Publishers,
101 Philip Drive, Assinippi Park, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers Group,
P.O. Box 322, 3300 AH Dordrecht, Holland

D. Reidel Publishing Company is a member of the Kluwer Academic Publishers Group

All Rights Reserved
© 1986 by D. Reidel Publishing Company, Dordrecht, Holland.

Softcover reprint of the hardcover 1st edition 1986

No part of the material protected by this copyright notice may be reproduced or utilized
in any form or by any means, electronic or mechanical, including photocopying, recording
or by any information storage and retrieval system, without written permission from the
copyright owner.

CONTENTS

Contributors.....	ix
Preface.....	xiii
1. A Theoretical Approach to Substituent Effects in radical Chemistry (G. Leroy, D. Peeters, M. Sana and C. Wilante)	1
2. Sigma and Pi Effects in Radicals (T. Clark).....	49
3. The Contrasting Strain Energies of Small Ring Carbon and Silicon Rings. The Relationship with Free Radical Energies (P. von Ragué Schleyer).....	69
4. Allylic and Allenic Capto-dative Stabilization in Nitrogen Centered Free Radicals (D. Kost, M. Raban and K. Aviram).....	83
5. Conformational Preferences in Beta Substituted Ethyl Radicals A Quantitative Analysis of Hyperconjugation, Homoconjugation, d-Orbital and Steric Effects (J. Fossey).....	87
6. Substituent Effects on the Thermochemistry and Electro-chemistry of Free Radicals (J.A. Hawari, J.M. Kanabus-Kaminska, D.D.M. Wayner and D. Griller).....	91
7. Some Applications of ESR Spectroscopy to the Study of Substituent Effects (G.W. Burton, L.J. Johnston, J.C. Walton and K.U. Ingold)....	107
8. Substituent Effects on Absolute Rate Constants and Arrhenius Parameters for the Addition of tert-Butyl Radicals to Alkenes (H. Fischer).....	123
9. Allylic Radicals - An ESR Spectroscopical Study (R. Sustmann).....	143
10. ESR-Spectroscopical Investigation of Capto-dative Substituent Effects in Benzyl Radicals (H.G. Korth, P. Lommes and R. Sustmann, L. Sylvander and L. Stella).....	167
11. The Effect of Substituents on Benzylic Radical ESR Hyperfine Coupling Constants. The σ_q^* Scale Based Upon Spin Delocalization (D.R. Arnold).....	171
12. Determination of Thermodynamic Stabilisation in Amino-Substituted Alkyl radicals (I. MacInnes, J.C. Walton and D.C. Nonhebel).....	189

13. Phosphinylhydrazyls $R_2N\dot{N}P(O)L_2$. Influence of the Phosphinyl Group on the 3-Electron $NN\pi^2$ Bond (P. Tordo).....	191
14. Substituent Effects on the Dimerization of Vinyl Nitroxides and on the Dissociation of Their Tricyclic Dimers (H.G. Aurich, O. Bubenheim and K.-D. Mogendorf).....	195
15. Substituent Effects on the CC-Bond Strength (H. Birkhofer, H.-D. Beckhaus and C. Rüchardt).....	199
16. The Different Recombinations of Diphenyl Methyl Radicals $Ph_2C^{\bullet}-R$, $R = tBu, CN, COOR', COR'$ (W.P. Neumann and R. Stapel).....	219
17. Some Chemistry of Radical Ions (J.M. Tedder).....	223
18. Substituent Effects on the Methylenecyclopropane Rearrangement. A Probe for Free Radical Effects (X. Creary).....	245
19. 2-Oxomorpholin-3-yl Radicals (T.H. Koch).....	263
20. Azoalkane Decompositions as Measures of Radical Substituent Effects (J.W. Timberlake).....	271
21. Orbital Effects in Carbohydrate Radicals (B. Giese, J. Dupuis, K. Gröninger, J. Hasskerl, M. Nix and T. Witzel).....	283
22. ESR-Spectroscopical Investigation of Carbohydrate Radicals in Solution. Radical Stabilization by Beta C-O Bonds (H.G. Korth and R. Sustmann, J. Dupuis, K.S. Gröninger, T. Witzel and B. Giese).....	297
23. Studies on the Captodative Effect. Entropy/Enthalpy Compensation as Solvent Effect in Radical Forming Reactions. A relative Radical Stabilisation Scale (R. Merényi, Z. Janousek and H.G. Viehe).....	301
24. $\sigma^{\bullet}$ Revisited (R.A. Jackson).....	325
25. Captodative Effect on the relative Rates of H-Abstraction by Tert-Butoxy Radicals (L. Vertommen, M. Beaujean, R. Merényi, Z. Janousek and H.G. Viehe).....	
26. Substituent Effects in Gas-Phase Thermal Hydroxylation and Hydrogenolysis (R. Louw, J.A. Manion and P. Mulder).....	
27. Heterocyclic Substituents in SRN1 Reactions (M.P. Crozet and P. Vanelle).....	
28. Substituent Effects on the Oxidation of Toluenes by Molecular Oxygen : The Surprising Reactivity of p-Methoxytoluene (M. Costantini and L. Krumenacker).....	
29. Free Radical Additions of Dichloromethane to δ -Alkenyl t-Butyl Peroxides (B. Maillard, M. Agorrodý and E. Montaudon).....	
30. The Non-Chain Radicaloid Mechanism of Some Nucleophilic Substitution Reactions (A.R. Katritzky).....	

31. Captodative Substituent Effects in Cycloaddition Reactions (L. Stella).....	361
32. Captodative Substitution Effect in [2+2]Cycloadditions Between Allenes and Olefins (G. Coppe-Motte, A. Borghese, Z. Janousek, R. Merényi and H.G. Viehe).....	371
33. Captodative Alkenes as Dipolarophiles - Kinetic Studies (D. Döpp and J. Walter).....	375
34. Captodative Alkenes in Concerted 1,3-Dipolar Cycloadditions (D. Döpp, J. Walter and S. Holz).....	379
35. Photo-Diels-Alder Addition of Two Captodative Alkenes to 1-Acetonaphtone (D. Döpp and H.R. Memarian).....	383
36. Free Radical Cyclization of Unsaturated Carbonic acid Deri- vatives (M.D. Bachi and E. Bosch).....	387
37. Synthetic Applications of the Polar Effects of the Substituents in Free-Radical Reactions (F. Minisci).....	391
38. Selectivity in Homolytic Aromatic Substitutions. Alkylations of Pyridines (M. Tiecco).....	435
39. The Invention of High-Yielding Radical Chain Reactions (D.H.R. Barton and Samir Z. Zard).....	443
40. Epilogue (R. Louw).....	463
Participants.....	467
Index.....	471

CONTRIBUTORS

Arnold Donald D., Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Aurich Hans G., Fachbereich Chemie der Philipps-Universität, Hans-Meerwein Strasse, D-3550 Marburg, Germany

Bachi Mario D., The Weizmann Institute of Science, Department of Organic Chemistry, 76100 Rehovot, Israel

Balaban A.T., Str.Poenaru Bordea 6, Apt13, R-70502 Bucharest Roumania.

Barton Sir Derek, Institut de Chimie des Substances Naturelles, CNRS, F-91190 Gif-sur-Yvette, France

Beckhaus Hans-Dieter, Institut für Organische Chemie und Biochemie, Universität Freiburg, Albertstrasse 21, D-7800 Freiburg 1, Germany

Citterio Attilio, Politecnico di Milano, Istituto di Chimica Piazza L. de Vinci 32 I-20133 Milano, Italy

Clark Timothy, Friedrich-Alexander Universität Erlangen-Nürnberg, Institut für Organ. Chemie, Henkestrasse 42, D-8520 Erlangen, Germany

Costantini M., Rhône-Poulenc Industries, Centre de Recherches de St. Fons, BP62, F-69190 Saint-Fons, France

Creary Xavier, Department of Chemistry, University of Notre Dame, Notre Dame IN 46556 U.S.A.

Crozet Michel P., Université de Droit, d'Economie et des Sciences Naturelles d'Aix-Marseille III. CNRS VA 109, Rue H. Poincaré, F-13397 Marseille Cedex 13, France

Döpp Dietrich, Universität Duisburg, Fachgebiet Organische Chemie Postfach 101629, D-4100 Duisburg 1, Germany

Fischer Hanns, Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstr.190, 8057 Zürich, Switzerland

Fossey Jacques, L.E.S.C.O.-C.N.R.S. 2 A 8, rue Henri Dunant, BP 28, F-94320 Thiais, France

Giese Bernd, Technische Hochschule Darmstadt, Institut für Organische Chemie, Petersenstrasse 22, D-6100 Darmstadt, Germany

Griller David, National Research Council of Canada, Division of Chemistry, Ottawa, Canada K1A 0R9

Ingold Keith U., National Research Council of Canada, Division of Chemistry, Ottawa, Canada K1A 0R9

Jackson Richard A., School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Great Britain

Janousek Zdenek, Université de Louvain, Laboratoire de Chimie Organique, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

Katritzky Alan R., University of Florida, Department of Chemistry, Gainesville, FL Florida 32611, U.S.A.

Koch Tad H., University of Colorado, Department of Chemistry and Biochemistry, Boulder Co 80309-0215, U.S.A.

Korth H.G., Institut für Organische Chemie, Universität Essen, GHS, D-4300 Essen 1, Germany

Kost Daniel, Ben Gurion University of the Negev, Department of Chemistry, Beer-Sheva 84105, Israel

Leroy George, Université de Louvain, Laboratoire de Chimie Quantique, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

Louw Robert, Center for Chemistry and the Environment Gorleaus Labs, The State University of Leiden, P.O. Box 9502, NL-2300 RA Leiden, The Netherlands

Maillard Bernard, CNRS VA 35, Laboratoire de Chimie Organique et Organométallique, Université de Bordeaux 1, 351 Cours de la Libération, F-33405 Talence-Cedex, France

Merényi Robert, Université de Louvain, Laboratoire de Chimie Organique, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

Minisci Francesco, Politecnico di Milano, Dipartimento di Chimica, Piazza L. da Vinci, 32, I-20133 Milano, Italy

Neumann Wilhelm P., Universität Dortmund, Otto-Hahn-Strasse, Postfach 50 05 00, D-4600 Dortmund 50, Germany

Rüchardt Christoph, Institut für Organische Chemie und Biochemie, Albertstrasse, 21, D-7800 Freiburg 1, Germany

Stella Lucien, Université de Droit, d'Economie et des Sciences Naturelles d'Aix-Marseille III, Laboratoire de Chimie Organique B, Rue Henri Poincaré, F-13397 Marseille Cedex 13, France

Sustmann Reiner, Institut für Organische Chemie, Universität-GHS Essen
Universitätsstrasse 5, D-4300 Essen 1, Germany

Tedder Lord John M., Department of Chemistry, University of St.
Andrews, St. Andrews Fife, KY16 9ST, United Kingdom

Tiecco Marcello, Istituto di Chimica Organica, Facolta di Farmacia,
Universita di Perugia , I-06100 Perugia, Italy

Timberlake Jack W., University of New Orleans, Department of Chemis-
try, Lakefront, New Orleans, LA 70122, U.S.A.

Tordo Paul, Université de Provence - Structure et Réactivité des
Espèces Paramagnétiques, C.N.R.S. UA 126, Rue H. Poincaré, F-13397
Marseille Cedex 4, France

Vertommen Luc, AKZO, Research Laboratories, Velperweg, 76, NL-6824 BM
Arnhem, The Netherlands

Viehe Heinz Gunter, Laboratoire de Chimie Organique, Université de
Louvain, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

von Ragué Schleyer Paul, Friedrich-Alexander-Universität Erlangen-
Nurnberg, Institut für Organische Chemie, Henkestrasse 42, D-8520
Erlangen, Germany

Walton John C., Department of Chemistry, University of St. Andrews,
St. Andrews Fife, KY16 9ST, United Kingdom

PREFACE

Respectably old radical chemistry which plays a major role in life-processes, both desired (breathing, ...) and non-desired (inflammatory diseases, ageing,...) has been gaining new youth in the past decade.

Modern spectroscopy and other physical methods, recent advances in computational methods as well as impressive and mechanistically well-understood syntheses have led to a number of spectacular developments in the field of radical chemistry. The impact of these achievements will reach far beyond the field of organic chemistry, for example into biology and medicine.

New facts and concepts in this rapidly expanding field deserved discussion among a number of leading experts present at the Workshop both for the information and constructive criticism. This happened during a particular brainstorming session and some of the impressions and reflections exchanged are recorded in the Epilogue.

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

We had the honour to organise this Workshop because some years ago, in collaboration with L. Stella, we became involved in radical stabilising effects when both a donor and an acceptor (captor) groups are present on a C-radical. This leads to an enhanced stabilisation which we called the captodative effect and we have endeavoured the first extensive investigation of this effect on carbon centered radicals. Nevertheless such an effect was intimated as early as in 1952 by Dewar, but it was not until about 20 years later when Katritzky provided some first experimental results and called this effect "merostabilisation". Similar effect on nitrogen-centered radicals has been discovered and well documented by Balaban under the name "push-pull" stabilisation. There has not yet been reached a complete agreement as to the extent of such an effect but by now more leading groups are active in this field. Owing to this concern it came to light that even the effect of a single substituent may still be subject to controversy. This explains why the organization of such a meeting was of paramount importance.

Thanks to a generous grant from NATO Scientific Affairs Division such a meeting among almost 50 specialists became possible at

Louvain-la-Neuve (Belgium). The lectures and posters were streamlined on the following topics :

- computations concerning both closed and open-shell species;
- kinetic and thermodynamic phenomena;
- ESR techniques;
- devising radical stabilising scales;
- new radical reactions in synthesis.

Many points have been clarified and those which still manage to escape our full understanding will stimulate the participants and, as we hope, the readers of this book to help to solve them.

H.G. Viehe,
Z. Janousek,
R. Merényi,

Louvain-la-Neuve, 1986.