

Methods for the Oxidation of Organic Compounds

Alkanes, Alkenes, Alkynes, and Arenes

(Best Synthetic Methods)

Alan H. Haines

(1)

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Foreword

There is a vast and often bewildering array of synthetic methods and reagents available to organic chemists today. Many chemists have their own favoured methods, old and new, for standard transformations, and these can vary considerably from one laboratory to another. New and unfamiliar methods may well allow a particular synthetic step to be done more readily and in higher yield, but there is always some energy barrier associated with their use for the first time. Furthermore, the very wealth of possibilities creates an information retrieval problem: How can we choose between all the alternatives, and what are their real advantages and limitations? Where can we find the precise experimental details, so often taken for granted by the experts? There is therefore a constant demand for books on synthetic methods, especially the more practical ones like "Organic Syntheses," "Organic Reactions," and "Reagents for Organic Synthesis," which are found in most chemistry laboratories. We are convinced that there is a further need, still largely unfulfilled, for a uniform series of books, each dealing concisely with a particular topic from a *practical* point of view—a need, that is, for books full of preparations, practical hints, and detailed examples, all critically assessed, and giving just the information needed to smooth our way painlessly into the unfamiliar territory. Such books would obviously be a great help to research students as well as to established organic chemists.

We have been very fortunate with the highly experienced and expert organic chemists who, agreeing with our objective, have written the first group of volumes in this series, "Best Synthetic Methods." We would always be pleased to receive comments from readers and suggestions for future volumes.

A.R.K., O.M.-C., C.W.R.

Preface

While I was collecting information for the contribution on oxidation to the Best Synthetic Methods Series, the need became clear, in view of the extremely wide range of oxidative methods employed by organic chemists, to divide the subject matter between two volumes in order to provide the practical information in a book of convenient size for use in the laboratory. This volume deals with the oxidation of hydrocarbons under the headings of alkanes (including alkyl groups and hydrocarbon residues), alkenes, alkynes, and arenes. A companion volume will deal with the oxidation of alcohols and related compounds, such as alkyl halides, alkyl sulphonates, and ethers, the oxidation of aldehydes and ketones, and the oxidation of 1,2-diols and related compounds. In addition, selectivity in the oxidation of polyfunctional compounds will be considered. No attempt is made in either volume to include oxidation at heteroatoms such as sulphur or nitrogen, unless it forms a part of an oxidative process of the type already described.

Most of the oxidative techniques considered here are illustrated with detailed experimental procedures taken from the literature. The original procedures have been edited and rewritten to ensure a uniformity of style. Although every attempt has been made to ensure that all pertinent information is included, consultation of the original literature may be advisable in some cases.

The number of experimental procedures that may be described fully is clearly limited by the availability of space, and, to alleviate this problem, tables which contain several examples of each type of oxidation are included. These tables, numbered so as to indicate the chapters with which they are associated, are placed together in an appendix. Each entry in a table summarizes an experiment for which, in nearly every case, a good, fully detailed procedure is described in the original reference.

I am indebted to Professor A. McKillop for reading critically the entire manuscript and for his valuable comments.

The writing of any book places considerable demands on the author's family. I can only express my sincere gratitude to my wife, Carol, for the support she has

given me in this task, thank her for the excellent job she did in typing the manuscript, and ask forgiveness from my children, Neal and Mark, for not spending sufficient time with them during a considerable part of the writing period.

ALAN H. HAINES

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TABLE 1.1

Some Simple Functional Groups Arranged According to Their Oxidation State

Increasing state of oxidation →				
RH	—C=C— ROH RCl RNH ₂ etc.	—C≡C— RCOR RCH=NOH R ₂ C—CR ₂ OH OH R ₂ C—CR ₂ Cl Cl etc.	RCO ₂ H RCO ₂ R RCONH ₂ RC≡N etc.	CO ₂ CCl ₄ etc.

inorganic chemistry are, generally, less easily applied in organic chemistry.* In this book the oxidative series shown in Table 1.1 is used as a basis for defining an oxidative transformation, and oxidation is classed as the conversion of a functional group to one of a higher category. Generally, compounds which are related by the addition or removal of a molecule of water or its equivalent are regarded as being in the same oxidation state, but this is not always the case. Thus, when the elements of water are removed from an aldoxime, a nitrile is produced and a change in oxidation level from an aldehyde to an acid is thereby achieved. On the other hand, dehydration of an amide to a nitrile causes no change in oxidation level.†

The replacement of an electronegative group at a carbon atom by another electronegative group, for example in the conversion of a geminal dichloride, RCHCl_2 , into a geminal diacetox compound $\text{RCH}(\text{OAc})_2$, causes no major change in the overall oxidation level of the carbon atom in the functional group. On the other hand, replacement of a hydrogen atom attached to carbon by a substituent that is more electronegative than hydrogen results in an oxidation at that carbon atom. Thus, the substitution of hydrogen in an alkane or arene by halogen, or the addition of halogen to an alkene are, strictly, oxidative processes. However, in common with most other books and review articles on oxidation, reactions of these types are not included unless they form an integral part of another oxidative process, as in the conversion of

* An earlier book on the oxidation of organic compounds (1) does, however, classify oxidations based on the number of electrons transferred to the oxidant.

† In the oxime to nitrile conversion the number of bonds from the electronegative nitrogen atom to the carbon atom of the functional group increases from two to three, but in both the amide and nitrile there are three bonds to the carbon atom from electronegative atoms (nitrogen and oxygen, and nitrogen, respectively).