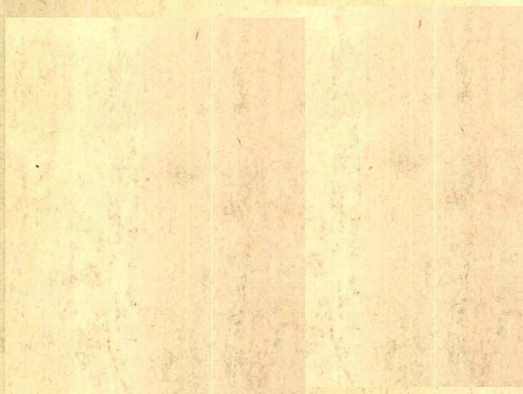


Studies in Organic Chemistry Vol. 9

ELECTROPHILIC ADDITIONS TO UNSATURATED SYSTEMS

P.B.D. de la Mare

R. Bollon



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PREFACE

Since 1966, when the first edition of this book was published, our knowledge of the detailed pathways concerned in addition reactions has been extended greatly, both by new experimental findings and by important reviews of special aspects where major developments have been made. The general framework of the first edition, however, remains in our view soundly based and useful: we have aimed to show relationships between observations covering a wide range of chemical phenomena in which an unsaturated compound reacts with an electrophilic reagent to form an intermediate or a transition state which has carbocationic character. Addition by saturation or partial saturation of the original multiple bond then may be a consequence of this carbocationic character.

In this new edition, even more than in the first, exhaustive treatment of the material has not been possible. We have tried to stress such general principles as we consider most important, and to draw attention to the most significant new experimental work and to relevant monographs and reviews. From the cited material we believe that the reader will be led into the existing literature relating to his or her specialised interests.

This book would not have been possible without criticism derived over many years from our seniors, colleagues, co-workers, and friends. We thank them all, and we thank also the University of Auckland and Bedford College (University of London) for periods of study leave essential to the completion of this revision.

We are greatly indebted to Mrs. Doris Storey, who typed the final copy and prepared the diagrams.

P.B.D. de la Mare

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and London, England.

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CHAPTER 1

INTRODUCTION; DEFINITIONS, AND CRITERIA FOR CLASSIFICATION

1.1. INTRODUCTION

Unsaturated compounds characteristically react by addition, in which a multiple bond is attacked by a reagent (the addendum) to form an adduct which has thus become partly or wholly saturated. The addition of bromine to ethylene (equation (1.1)) is typical:



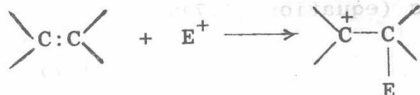
The term *addition* is used to describe a reaction in which both atoms of the multiple bond are attacked in such a way as to decrease the multiplicity of the bond; olefins therefore give saturated compounds (equation (1.1)) and acetylenes give olefins analogously (equation (1.2)).



The product need not be stable in the sense that it can be isolated, nor in the sense that it is the final product of the sequence in which we are interested; but it must be at least a true intermediate on the reaction path, and correspond with a minimum in the profile of free energy against reaction coordinate.

Both the above reactions (equations (1.1) and (1.2)) are *vic-*, or *1,2-*, additions. These should be distinguished from *1,1-*, *1,3-*, and other modes of addition in which the reagent provides two new covalent bonds to the substrate. However, this review is concerned mainly with *1,2-* additions, and the prefix shall only be used where there may be confusion with the other modes.

The formation of one covalent bond, by a reversal of a heterolytic process, is in Ingold's terminology [1] a *co-ordination reaction*. Equation (1.3), in which E^+ represents a general electrophile, therefore does not qualify as an addition which has only occurred after subsequent reaction with a nucleophile.



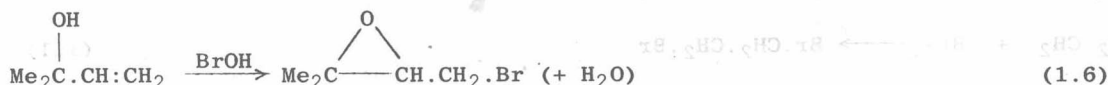
Likewise equation (1.4) is not an example of an addition, since only a loose complex (a π -complex) is formed between the olefin and the electrophile; the double bond is perturbed, but not saturated:



The formation of a cyclic structure (equation (1.5)), however, is an addition within our definition.



As two bonds are formed to carbon during an addition, they may form either synchronously or in a multi-stage process; it is equally acceptable that either bond may arise from an intramolecular attack. Thus, the reaction shown in equation (1.6) is an addition in which the nucleophile is provided intramolecularly [2].



The dividing line between complex formation and addition is a narrow one (cf. equations (1.4) and (1.5)) because of the difficulty in defining at what stage the π -electrons are merely perturbed by the reagent without forming a covalent bond with it. However, the distinction is useful, even if sometimes difficult to draw experimentally. There are, indeed, good precedents for making such a ruling; Huisgen *et al.* [3] did so when they excluded the formation of complexes between olefins and silver ions from their classification of cyclo-additions.

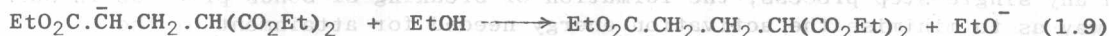
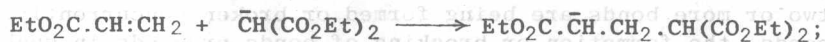
1.2 SCOPE OF THE WORK

This book deals primarily with homogeneous reactions in solution; although the related heterogeneous processes and their corresponding eliminations are of considerable theoretical and technical importance, little reference is made to them.

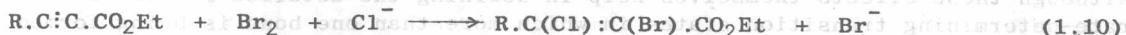
There are three main, mechanistically useful, divisions. Firstly, homolytic additions include all processes in which the addition is initiated by a free radical; they are often characterised by the development of a chain process in which the initiating radical is regenerated and in which one act of homolytic fission produces many molecules of product. Peroxide-induced additions of hydrogen bromide to olefins are well-known examples (equation (1.7)).



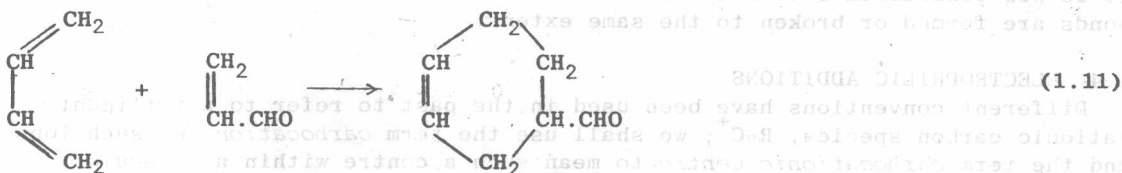
Secondly, heterolytic additions arise when the first new bond formed to the unsaturated compound involves the co-ordination of reagent to substrate, or of substrate to reagent, through the donation of an electron pair. In the following examples (sequences (1.8) and (1.9)) the role of the reagent as generalised acid (electrophile) or as generalised base (nucleophile) may be identified:



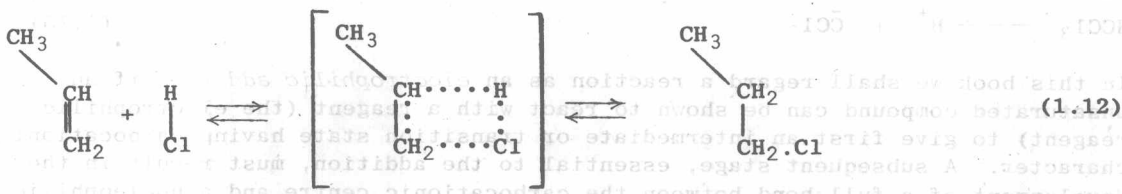
Consideration of the termolecular process formulated in equation (1.10) suggests the possible existence of a heterolytic addition in which the two new bonds are formed concurrently in a concerted process (see section 1.13).



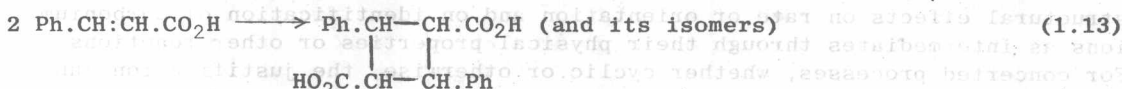
Thirdly, cyclic additions may occur, in which the two new bonds which complete the addition process are formed in a concerted fashion through a *cyclic* transition state. The Diels-Alder reaction (equation (1.11)), which involves 1,4-addition with rearrangement in one unsaturated substrate and 1,2-addition in another, is a well-known example in which both the transition state and the product are cyclic.



It is not impossible, however, for a reaction involving a cyclic transition state to give an acyclic product. An example is provided by the equilibrium shown in equation (1.12), which in the gas phase can be established through a cyclic transition state [4].



Cyclic additions in general may have a wide range of transition states; some have characteristics of radical processes, as in photochemically activated additions. Equation (1.13) gives an example of a reaction which can be activated in this way, and under these conditions is homolytic in nature.



1.3 CONCERTED PROCESSES

Equations (1.10) and (1.11) provide examples of reactions which are described as *concerted* because two or more bonds are being formed or broken concurrently. In any single-step process, the formation or breaking of bonds proceeds in such a way as to minimise the activation energy needed for attainment of the transition state. The resulting partial bonds are not necessarily all formed or broken to the same extent in the transition state. Indeed, in the general case the reverse is true. Consequently it is not possible to predict, *a priori*, what effect substituents or solvents may have on the rates of such reactions, although these effects themselves help in defining the detailed structure of rate-determining transition states in which more than one bond is being formed or broken. For some replacements and eliminations, attempts have been made to obtain more definitive information from studies of heavy-atom isotope effects [5] for all the atomic centres involved, but so far there is very little information of this kind available for addition reactions. Theoretical calculations of energies of atomic assemblies, which in principle could provide the necessary information, in practice have not yet been developed sufficiently.

The term "*synchronous*" has sometimes been used as a synonym for "*concerted*"; it is now considered better to restrict the former to reactions in which the new bonds are formed or broken to the same extent.

1.4 ELECTROPHILIC ADDITIONS

Different conventions have been used in the past to refer to a triligant cationic carbon species, R_3C^+ ; we shall use the term *carbocation* for such ions and the term *carbocationic centre* to mean such a centre within a molecule, irrespective of its charge-type. The related species, $R_2C:C(R)^+$ and $R.C:C^+$, are likewise carbocations. Both co-ordination (equations (1.8) and (1.9)) and heterolysis (equations (1.14) and (1.15)) can form carbocations or carbanions.



In this book we shall regard a reaction as an *electrophilic addition* if an unsaturated compound can be shown to react with a reagent (the electrophilic reagent) to give first an intermediate or transition state having carbocationic character. A subsequent stage, essential to the addition, must result in the development of a full bond between the carbocationic centre and a nucleophilic centre. The sequence shown in (1.8) is an example; the relative rates of the various processes which make up the addition and its reverse are regarded as irrelevant to the classification.

Evidence to support the inclusion of a particular reaction within our classification is for some reactions very strong, and may be based upon structural effects on rate or orientation and on identification of carbonium ions as intermediates through their physical properties or other reactions. For concerted processes, whether cyclic or otherwise, the justification can become a matter for argument; we shall put particular weight upon the information derived from the effect of change in structure and of the environment on the rate of the reaction. Reactions for which we believe the evidence supports the view that the intermediate is carbanionic in character

shall not be discussed as a separate group, and cyclic additions shall be discussed only for those cases in which structural effects, or other reactions, appear to show the carbocationic nature of the transition state to be well developed.

For sub-classification, it is convenient to use the position in the Periodic Table of the element which becomes electrophilically bound to an atom of the multiple bond. Electrophiles of different charge-types will be met, particularly cations and neutral molecules; we shall also encounter reaction paths leading to *syn*-addition (where reagents attach themselves to the same side of the multiple bond) and those which conversely give *anti*-addition.

1.5 EFFECTS OF SUBSTITUENTS UPON REACTIVITY

Two related, but not identical, methods are used to describe the effects of substituents upon reactivity.

The first (the qualitative theory) uses Ingold's concepts and terminology [1]. *Steric effects* are first differentiated from *polar effects*. The first arise from the bulk of the substituent, and can in principle result in either *steric acceleration* or *steric retardation* (steric hindrance) of a reaction. *Primary steric effects* are those in which the bulk of the substituent affects reactivity by its direct influence upon the reacting centre. *Secondary steric effects* arise when the substituent, through its bulk, changes the effect (either steric or polar) of another substituent which influences the reacting centre. *Stereo-electronic effects* arise when the electronic movements in the transition state have special geometric requirements which are influenced by restrictions of movement within the reacting molecule.

Polar effects themselves can be divided into two main classes: those of electrostatic induction (inductive effects: symbol, $\pm I$) and those involving electronic delocalisation (conjugative effects: symbol, $\pm K$). A positive sign refers to electron-release to the reaction centre; conversely, a negative sign describes electron-withdrawal. Both of these effects vary with the system and the reaction, and so sometimes an attempt is made to distinguish between effects of *polarisation*, which reflect only the properties of the ground state of the organic molecule and its influence on the transition, and effects of *polarisability*, by which the influences specific to the acquisition of particular transition states is described. Differentiation between these two types of structural influence is experimentally difficult, so we shall not normally attempt to make the distinction; some of the problems involved are discussed by de la Mare and Ridd [6].

The second approach to the effects of substituents upon reactivity uses linear free energy relationships. The Hammett equation [7] takes the form of equation (1.16) where k^R is the rate coefficient for some substrate in which R is the generalised substituent influencing the rate of reaction (k^H) at one site of the unsubstituted compound; σ_R is a substituent constant defined as $\log_{10}(K_a^R \cdot C_6H_4 \cdot CO_2H / K_a^H \cdot C_6H_5 \cdot CO_2H)$, where $K_a^R \cdot C_6H_4 \cdot CO_2H$ is the dissociation constant of the correspondingly substituted benzoic acid under standard conditions; and ρ is the slope of the plot of $\log_{10}(k^R/k^H)$ against σ_R .

$$\log_{10}(k^R/k^H) = \sigma_R \cdot \rho \quad (1.16)$$