



# **GLOSSARY OF ORGANIC CHEMISTRY**

**Including Physical Organic Chemistry**

by

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*The Hebrew University of Jerusalem*

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## PREFACE

The present book was written mainly for the use of those who are not specialists (or not *yet* specialists) in Organic and Physical Organic Chemistry, but who have need and occasion to use the relevant literature. Thus, workers in fields related to Organic Chemistry, such as in Inorganic, Analytical, Physical, Biological and Industrial Chemistry, as well as in Physics, Medicine, Biology and Agriculture, often have to refer to textbooks or original papers in Organic Chemistry and, due to the extensive specialization in the terminology of the latter, may find it difficult to understand the material. The same is true for students of chemistry, who learn primarily the terminology used by their teachers but have no opportunity to get acquainted with terms used by other schools.

It is hoped that this book will fill the need for those mentioned above and will also be useful as a memory refresher, as well as a simplified short-cut reference source to the secondary literature of text-books and review articles.

Several classes of terms had to be practically left out. Only a very few analytical methods and colour tests have been included and the choice of these has been more or less a matter of personal preference. Thus a few terms like permanganate test, Dumas method, etc., have been included while others, possibly equally important, may be missing. The choice of "Name Reactions" was governed by the consideration that their usage is very often historically inexact, confusing and generally deplorable, giving no mnemotechnic aid for the student. Accordingly, the term "diene synthesis" should be preferred to "Diels-Alder reaction." Nevertheless, as the use of names of chemists for many reactions is deeply entrenched in the literature of Organic Chemistry, it was felt that these had to be included in the book. Hence, name reactions which are referred to as such in textbooks and in the review literature were included, but those which are generally used only in the original specialized research literature were omitted. Obviously, the decision was often not only difficult but also rather arbitrary.

The sign (\*) after an expression shows that a definition or explanation of this term appears in the book at the proper alphabetical place for the term. If several synonyms are used in the literature for the same concept, cross references are included for each. These synonyms also appear in brackets after the term where the definition is given.

I should be very grateful if mistakes and omissions are brought to my notice, and every effort will be made to correct them in future editions.

It is a pleasure to acknowledge the help, encouragement and good advice given to me by Prof. E. D. Hughes, F.R.S. I also wish to thank Dr. Paul Rosbaud for his help and kindness and, last but not least, my wife who

suffered silently and without complaint long days and evenings when I kept myself incommunicado.

The Hebrew University  
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March, 1961

SAUL PATAI

## INTRODUCTION

Students of all ages who aspire to read the literature of a subject in which they are not immediately familiar are often bedevilled by the use of strange words and phrases which constitute the jargon of the specialization. Ordinarily, one may quickly remedy a defect by recourse to a dictionary. But, hitherto, a suitable Glossary of chemical terms has not been available on a sufficiently broad basis. Dr. Saul Patai's aim has been to correct this situation in the field of organic chemistry. The general problem, which is so easily stated, is difficult to solve, but the author of this volume has made a most valuable contribution in his chosen subject and the book can be recommended to a wide circle of chemists.

E. D. HUGHES.

## KEY TO THE REFERENCES

Review Publications are referred to by the capital letters of their titles, followed by the volume number and by the number of the page on which the review starts.

Other books are divided into sections according to their subject matter and referred to by a capital letter (showing to which group the book quoted belongs, e.g. **A** for general organic textbooks, **B** for textbooks of physical and theoretical organic chemistry, etc.) and by the serial number of the book within its group, e.g. **C 5** refers to book number 5 in Section C below).

As the books quoted contain adequate subject indices, the page numbers are generally omitted so as to save space. Page numbers in the books referred to are given in some cases, e.g. if the entry appears in the index of the book under a different name or if it does not appear in the index at all, although the subject is treated in the text.

Omission of a textbook or any other publication from the books chosen for the references should on no account be taken as an expression of criticism. The literature of Organic Chemistry is so large that only a small (although, it is hoped, representative) fraction of the books covering practically identical subject matter could be scanned, and only these were included in the list. In consequence, most probably books of equal or larger merit were omitted from the lists.

In many cases the reference is to a whole section of the list, e.g. **A 1-16** means that the entry is discussed in *most* general textbooks of Organic Chemistry. This does not necessarily mean that *all* sixteen books quoted do discuss the entry in question, but it means that a large majority of them do, as well as a large majority of similar textbooks not included in the list.

### Review Publications

- CR** *Chemical Reviews* (published for the American Chemical Society).  
**QR** *Quarterly Reviews* (published by the Chemical Society, London).  
**OR** *Organic Reactions* (R. Adams, editor; Vols. I-X, Wiley).  
**AOC** *Advances in Organic Chemistry* (R. A. Raphael, E. C. Taylor and H. Wynberg, editors; Vols. 1-2, 1960, Interscience).

### A. General Textbooks of Organic Chemistry

- A 1** J. H. Conant and A. H. Blatt, *Chemistry of Organic Compounds*, 5th ed., 1959, 652 pp, Macmillan.  
**A 2** D. J. Cram and G. S. Hammond, *Organic Chemistry*, 1959, 712 pp, McGraw-Hill.

- A 3 G. M. Dyson, *A Manual of Organic Chemistry*, Vol. I ("Compounds of C, H, O and the Halogens"), 1950, 984 pp, Longmans, Green & Co.
- A 4 L. F. Fieser and M. Fieser, *Basic Organic Chemistry*, 1959, 378 pp Heath & Co.
- A 5 L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd ed., 1956, 1117 pp, Heath & Co.
- A 6 I. L. Finar, *Organic Chemistry*, Vol. I, 3rd ed., 1959, 822 pp; Vol. II, 2nd ed., 1959, 813 pp; Longmans, Green & Co.
- A 7 R. C. Fuson, *Advanced Organic Chemistry*, 1950, 669 pp, Wiley.
- A 8 R. C. Fuson and H. R. Snyder, *Organic Chemistry*, 2nd ed., 1954, 544 pp., Wiley
- A 9 W. J. Hickinbottom, *Reactions of Organic Compounds*, 3rd ed., 1957, 608 pp, Longmans, Green & Co.
- A 10 P. Karrer, *Organic Chemistry*, 4th ed., 1950, 983 pp, Elsevier.
- A 11 J. Packer and J. Vaughan, *A Modern Approach to Organic Chemistry*, 1958, 973 pp, Oxford.
- A 12 E. H. Rodd, *Chemistry of Carbon Compounds*, Vols. I-IV, 1951-1959, Elsevier.
- A 13 J. Schmidt, H. Gordon Rule and N. Campbell, *A Textbook of Organic Chemistry*, 6th ed., 1950, 947 pp, Gurney and Jackson.
- A 14 E. E. Turner and M. M. Harris, *Textbook of Organic Chemistry*, 1952, 904 pp, Longmans, Green & Co.
- A 15 E. Wertheim and H. Jeskey, *Introductory Organic Chemistry*, 3rd ed., 1956, 476 pp, McGraw-Hill.
- A 16 F. C. Whitmore, *Organic Chemistry*, 2nd ed., 1951, 1005 pp, Van Nostrand.

## B. Textbooks of Physical and Theoretical Organic Chemistry

- B 1 G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry*, 1941, 523 pp, Prentice-Hall.
- B 2 E. S. Gould, *Mechanism and Structure in Organic Chemistry*, 1959, 800 pp, Holt,
- B 3 L. Hammett, *Physical Organic Chemistry*, 1940, 404 pp, McGraw-Hill.
- B 4 P. H. Hermans, *Theoretical Organic Chemistry*, 1954, 507 pp, Elsevier.
- B 5 J. Hine, *Physical Organic Chemistry*, 1956, 497 pp, McGraw-Hill.
- B 6 W. Huckel, *Theoretical Principles of Organic Chemistry*, Vol. I, 1955, 916 pp; Vol. II, 1958, 1058 pp; Elsevier.
- B 7 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 1953, 828 pp, Cornell.
- B 8 E. Muller, *Neuere Anschauungen der Organischen Chemie*, 1957, 550 pp, Springer.
- B 9 W. A. Waters, *Physical Aspects of Organic Chemistry*, 5th ed., 1954, 539 pp, Van Nostrand.
- B 10 G. W. Wheland, *Advanced Organic Chemistry*, 3rd ed., 1960, 823 pp, Wiley.



**C. Monographs, Mainly Descriptive**

- C 1 A. Albert, *Heterocyclic Chemistry*, 1959, 500 pp, Oxford.
- C 2 K. W. Bentley (editor), *The Chemistry of Natural Products*, Interscience.  
Vol. 1, K. W. Bentley, *The Alkaloids*, 1958, 245 pp.  
Vol. 2, P. de Mayo, *Mono- and Sesquiterpenoids*, 1959, 328 pp.  
Vol. 3, P. de Mayo, *The Higher Terpenoids*, 1959, 248 pp.  
Vol. 4, K. W. Bentley, *The Natural Pigments*, 1960, 314 pp.  
Vol. 5, S. F. Dyke, *The Carbohydrates*, 1960, 242 pp.
- C 3 F. W. Billmeyer, *Textbook of Polymer Chemistry*, 1957, 518 pp, Interscience.
- C 4 J. W. Cook (editor), *Progress in Organic Chemistry*, Vols. I-III, 1952-1955, Butterworths.
- C 5 G. F. D'Alelio, *Fundamental Principles of Polymerization*, 1952, 517 pp, Wiley.
- C 6 R. C. Elderfield (editor), *Heterocyclic Compounds*, Vols. I-VII, 1950-1960, Wiley.
- C 7 P. Flory, *Principles of Polymer Chemistry*, 1953, 672 pp, Cornell.
- C 8 H. Gilman (editor), *Organic Chemistry*, Vols. I-IV, 2nd ed., 1942-1953, Wiley.
- C 9 G. L. Jenkins, W. H. Hartung, J. B. Data and K. E. Hamlin, *The Chemistry of Organic Medicinal Products*, 4th ed., 1957, 569 pp, Wiley.
- C 10 M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-metallic Substances*, 1954, 1384 pp, Prentice-Hall.
- C 11 N. Kharasch, *Organic Sulphur Compounds*, Vol. I, 1960, 400 pp, Pergamon.
- C 12 G. M. Kosolapoff, *Organophosphorus Compounds*, 1950, 376 pp, Wiley.
- C 13 H. Mark, C. S. Marvel, H. W. Melville and G. S. Whitley, *High Polymers*, Vols. I-XI, 1940-1956, Interscience.
- C 14 E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, 1957, 344 pp, Wiley.
- C 15 N. V. Sidgwick, *The Organic Chemistry of Nitrogen*, 1942, 590 pp, Oxford.
- C 16 C. A. Thomas, *Anhydrous Aluminium Chloride in Organic Chemistry*, 1941, 972 pp, Reinhold.
- C 17 A. Weissberger (editor), *The Chemistry of Heterocyclic Compounds. A Series of Monographs*, Vols. I-XIV, 1950-1960, Interscience.
- C 18 S. T. Yoffe and A. N. Nesmeyanov, *A Handbook of Magnesium Organic Compounds*, Vols. I-III, 1956, 2070 pp, Pergamon.

**D. Monographs, Mainly Physical and Theoretical**

- D 1 R. P. Bell, *Acid-Base Catalysis*, 1941, 211 pp, Oxford.
- D 2 R. P. Bell, *The Proton in Chemistry*, 1960, 223 pp, Cornell.
- D 3 J. G. Burr, *Tracer Applications for the Study of Organic Reactions*, 1957, 291 pp, Interscience.

- D 4** A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, 2nd Ed., 1961; 405 pp, Wiley.
- D 5** D. Ginsburg (editor), *Non-Benzenoid Aromatic Compounds*, 1959, 542 pp, Interscience.
- D 6** C. K. Ingold, *Introduction to Structure in Organic Chemistry*, 1956, 200 pp, Bell.
- D 7** W. Klyne and P. B. D. de la Mare, *Progress in Stereochemistry*, Vols. I-II, 1954-1958, Butterworths.
- D 8** J. E. Leffler, *The Reactive Intermediates of Organic Chemistry*, 1956, 275 pp, Interscience.
- D 9** P. B. D. de la Mare and J. Ridd, *Aromatic Substitution*, 1959, 252 pp, Butterworths.
- D 10** L. Melander, *Isotope Effects on Reaction Rates*, 1960, 181 pp, The Ronald Press.
- D 11** M. S. Newman (editor), *Steric Effects in Organic Chemistry*, 1956, 710 pp, Wiley.
- D 12** L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., 1960, 664 pp, Cornell.
- D 13** V. J. Shrinier and E. Campaigne (editors), *Conference on Hyperconjugation*, 1959, 176 pp, Pergamon.
- D 14** *Theoretical Organic Chemistry* (I.U.P.A.C. Kekulé Symposium), 1959, 298 pp, Butterworths.
- D 15** C. Walling, *Free Radicals in Solution*, 1957, 631 pp, Wiley.
- D 16** W. A. Waters, *The Chemistry of Free Radicals*, 1946, 295 pp, Oxford.
- D 17** W. A. Waters (editor), *Vistas in Free Radical Chemistry*, 1959, 264 pp, Pergamon.
- D 18** G. W. Wheland, *Resonance in Organic Chemistry*, 1955, 846 pp, Wiley.
- D 19** G. H. Williams, *Homolytic Aromatic Substitution*, 1960, 133 pp, Pergamon.

### E. Synthesis and Laboratory Technique

- E 1** N. D. Cheronis, *Micro and Semimicro Methods*, 1954, 628 pp, Interscience (Vol. VI of E 15).
- E 2** N. D. Cheronis, *Semimicro Experimental Organic Chemistry*, 1958, 410 pp, Hadrian Press.
- E 3** L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., 1957, 364 pp, Heath & Co.
- E 4** L. Gattermann, *Laboratory Methods of Organic Chemistry*, 1952, 435 pp, Macmillan.
- E 5** Houben-Weyl, *Methoden der Organischen Chemie*, Vols. I-IV, 4th ed., Georg Thieme.
- E 6** R. P. Linstead, J. A. Eldridge and M. Whalley, *A Course in Modern Techniques of Organic Chemistry*, 1955, 190 pp, Butterworths.
- E 7** V. Migrdichian, *Organic Synthesis*, Vols. 1-2, 1957, 1822 pp, Reinhold.
- E 8** *Newer Methods of Preparative Organic Chemistry*, 1948, 657 pp, Interscience.

- E 9 *Organic Syntheses*, Coll. Vol. I (ed., H. Gilman and A. H. Blatt), 1953, 692 pp, Wiley; Coll. Vol. II (ed., A. H. Blatt) 1943, 654 pp, Wiley; Coll. Vol. III (ed., E. C. Horning) 1955, 890 pp, Wiley.
- E 10 D. A. Shirley, *Preparation of Organic Intermediates*, 1951, 328 pp, Wiley.
- E 11 W. Theilheimer, *Synthetic Methods of Organic Chemistry*, Vols. I–XIV, 1946–1960, Interscience.
- E 12 A. I. Vogel, *Elementary Practical Organic Chemistry*, 1958, 980 pp, Longmans, Green & Co.
- E 13 R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, 1953, 887 pp, Wiley.
- E 14 A. Weissberger (editor), *Physical Methods of Organic Chemistry*, 3rd ed., Vol. I, Parts I–IV, 1959–60, 3539 pp, Interscience (Vol. I of E 15).
- E 15 A. Weissberger (editor), *Technique of Organic Chemistry*, Interscience.  
 Vol. II, *Catalytic, Photochemical and Electrolytic Reactions*, 2nd ed., 1956, 556 pp.  
 Vol. III, Part I, *Separation and Purification*, 1956, 883 pp.  
 Vol. III, Part II, *Laboratory Engineering*, 1957, 401 pp.  
 Vol. IV, *Distillation*, 1951, 668 pp.  
 Vol. V, *Adsorption and Chromatography*, 1951, 360 pp.  
 Vol. VII, *Organic Solvents*, 1955, 560 pp.  
 Vol. VIII, *Investigations of Rates and Mechanisms*, 1953, 784 pp.  
 Vol. IX, *Chemical Applications of Spectroscopy*, 1956, 812 pp.  
 Vol. X, *Fundamentals of Chromatography*, 1957, 465 pp.
- E 16 C. Weygand, *Organic Preparations*, 1945, 534 pp, Interscience.
- E 17 K. B. Wiberg, *Laboratory Technique in Organic Chemistry*, 1960, 260 pp, McGraw-Hill.

## F. Qualitative Organic Analysis

- F 1 E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, 1955, 810 pp, Academic Press.
- F 2 N. D. Cheronis and J. B. Entrikin, *Semimicro Qualitative Organic Analysis*, 2nd ed., 1957, 774 pp, Interscience.
- F 3 F. Feigl, *Spot Tests in Organic Analysis*, 5th ed., 1956, 619 pp, Van Nostrand.
- F 4 F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, 1949, 740 pp, Academic Press.
- F 5 M. Frankel and S. Patai, *Tables for Identification of Organic Compounds*, 1960, 239 pp, Chemical Rubber.
- F 6 Houben-Weyl, *Methoden der Organischen Chemie*, vol. II, 4th ed., 1953, George Thieme.
- F 7 E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds*, 1941, 691 pp, Wiley.
- F 8 S. M. McElvain, *The Characterization of Organic Compounds*, 1953, 303 pp, Macmillan.

- F 9 R. L. Shriner, R. C. Fuson and D. Y. Curtin, *Systematic Identification of Organic Compounds*, 4th ed., 1956, 426 pp, Wiley.
- F 10 F. Wild, *Characterization of Organic Compounds*, 2nd ed., 1958, 306 pp, Cambridge.

### G. Quantitative Organic Analysis

- G 1 S. J. Clark, *Quantitative Methods of Organic Microanalysis*, 1956, 253 pp, Butterworths.
- G 2 J. S. Fritz and G. S. Hammond, *Quantitative Organic Analysis*, 1957, 303 pp, Wiley.
- G 3 J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger (editors), *Organic Analysis*, Vols. I-IV, 1953-1960, Interscience.
- G 4 J. B. Niederl and V. Niederl, *Micromethods of Quantitative Organic Analysis*, 1942, 347 pp, Wiley.
- G 5 S. Siggia, *Quantitative Organic Analysis*, 2nd ed., 1954, 227 pp, Wiley.
- G 6 A. Steyermark, *Quantitative Organic Microanalysis*, 1951, 389 pp, Blakiston.
- G 7 K. G. Stone, *Determination of Organic Compounds*, 1956, 233 pp, McGraw-Hill.

### H. Literature of Chemistry

- H 1 E. J. Crane, A. M. Patterson and E. B. Marr, *A Guide to the Literature of Chemistry*, 2nd ed., 1957, 397 pp, Wiley.
- H 2 F. M. Dyson, *A Short Guide to Chemical Literature*, 2nd ed., 1958, 157 pp, Longmans, Green & Co.
- H 3 M. G. Mellon, *Chemical Publications*, 3rd ed., 1958, 327 pp, McGraw-Hill.

### Absolute configuration

The position in space of the four different groups surrounding an asymmetrical (\*) carbon atom has been determined experimentally only for a very few compounds. The term "absolute configuration" is used for the cases where this is actually known, although no generally accepted system of notation is in use as yet. It should be remembered that the various signs used for optical isomers (*d*, *D*, *l*, *L*, +, -) denote either actual optical rotations or configurations relative to an agreed reference substance and *not* absolute configurations.

AOC Vol. I, 304; A 2; A 11; B 10; D 7.

**Absorbance.** See Lambert-Beer law.

### Abstraction reaction (Hydrogen abstraction reaction)

The abstraction of an atom (especially hydrogen) from an organic molecule by a free radical (\*) with the formation of a new free radical from the molecule attacked:

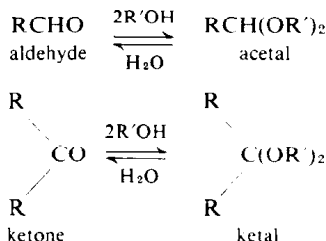


D 14, 262; QR XIV, 338.

**Acceptor.** See Electron acceptor.

### Acetal and ketal formation

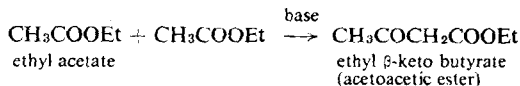
The formation of dialkoxy compounds from carbonyl compounds and alcohols, e.g.



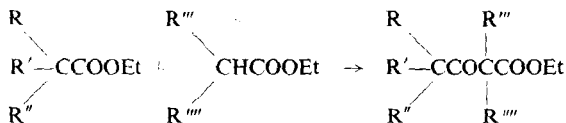
A 1-16.

**Acetoacetic ester condensation (Claisen reaction)**

Formation of a  $\beta$ -keto ester by the base-catalysed acylation (\*) of an ester having an  $\alpha$ -hydrogen atom with a second molecule of the same ester (or with a molecule of a different ester); e.g.



or, in general:



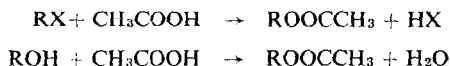
The presence of an  $\alpha$ -hydrogen is necessary only in one of the reacting ester molecules. The most widely used basic catalyst is sodium ethoxide, but other alkoxides, triphenylmethyl sodium, sodium amide, etc. are also effective. Yields are fair to good in the case of self-condensations (i.e. when both reacting esters are identical) and generally somewhat less good in reactions between two different esters.

A variation of the method is the Dieckmann reaction (\*).

OR I, 266; A 1-16; B 1;10.

**Acetolysis**

Solvolysis (\*) by acetic acid, e.g.

**Acetylation**

Acylation (\*) by acetyl ( $\text{CH}_3\text{CO-}$ ) groups.

**Acetylene coupling.** See Glaser coupling.

**Acid.** See Lewis acids, Lowry-Brönsted definition, Organic acids.

**Acid-base catalysis (Brönsted catalysis law)**

Many chemical reactions are catalysed by acids or bases. The general theory of acid-base catalysis proposed by Brönsted states that the velocity of a catalysed reaction is proportional to the concentration of the acid or base

present, where the terms "acid" and "base" are defined according to the Lowry-Brönsted definition (\*), including many other species apart from the hydrogen and hydroxyl ions.

The specific (hydrogen-ion) acid catalysis and the specific (hydroxyl-ion) base catalysis are special cases of the general acid-base catalysis.

**CR 5, 231; CR 10, 213; B 1-10; D 1; D 2; D 4; D 8.**

### Acidity constant

The equilibrium constant for the ionization of an acid HB in water, defined by the equation

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]}$$

The acidity constant is often given (in analogy to pH) in the logarithmic form

$$\text{p}K_a = -\log_{10} K_a$$

$K_a$  is a measure of the strength of an acid. Strong acids have high  $K_a$  values and low  $\text{p}K_a$  values.

**B 2; B 5; B 7; B 10; D 1; D 2.**

### Acidity function ( $H_0$ , Hammett acidity function)

The acidity function is a measure of the protonating ability of a solution, or, in other words, the tendency of a solution to donate a proton to an uncharged solute molecule. It is defined by the equation

$$H_0 = \text{p}K_{\text{BH}^+} - \log (C_{\text{BH}^+}/C_{\text{B}})$$

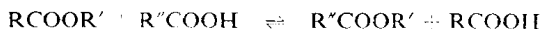
where  $C_{\text{B}}$  is the concentration of an indicator,  $C_{\text{BH}^+}$  the concentration of the same indicator in its protonated form, and  $K_{\text{BH}^+}$  the ionization constant of  $\text{BH}^+$ .

The study of the dependence of reaction rates on acidity-function values can often give valuable information relating to the mechanism of the reaction, e.g. it is assumed that a reaction in which there is a linear relationship between  $H_0$  and  $\log k$  has a unimolecular rate-determining step involving a protonated species of the reactant.

**CR 57, 1; CR 57, 935; B 1-10; D 1; D 2.**

### Acidolysis

The solvolytic reaction of an ester with a carboxylic acid, generally with the use of a strong acid catalyst, to form the ester of the second acid:



See also Solvolysis.

**Activated complex.** See Transition state.

**Activation energy** (Energy of activation, Arrhenius activation energy)

The difference between the potential energy of a reacting system in its initial state and its transition state (\*). This is the amount of energy the system has to acquire in order to be able to react. Reactions requiring high activation energies are usually slow and *vice versa*.

See also Arrhenius equation.

**B 1-10;** Textbooks of Physical Chemistry.

**Active mass.** See Activity.

**Active methylene group**

A methylene group ( $-\text{CH}_2-$ ) in which the hydrogen atoms are mobile and reactive. Any electron-attracting group ( $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOR}$ ,  $-\text{CO}$ ) adjacent to the methylene groups activates the latter, i.e. compounds like  $\text{CH}_2(\text{CN})_2$ ,  $\text{CH}_2(\text{COOR})_2$ ,  $\text{NCCH}_2\text{COOR}$  enter various reactions with ease (aldol condensations, Perkin, Knoevenagel, Doebner reactions, malonic ester syntheses, etc.).

**A 1-16; B 1-10**

**Activity** (Activity coefficient, Active mass)

In the rate of a reaction or in reaction equilibria, the rate coefficients ( $k$ ) or equilibrium constants ( $K$ ) are usually given in terms of the concentrations of the reactants and products. This is not strictly true: both  $k$  and  $K$  depend on the *activities* of the substances involved. The activities are defined by the equation  $a = fc$ , where  $a$  is the activity,  $f$  is the activity coefficient and  $c$  is the actual stoichiometric concentration. The value of  $f$  is equal to unity in very dilute solutions and in "ideal" solutions only; in many cases the value is close to unity so that calculations can be made using concentrations, but in order to obtain rigorously correct values the activity coefficients have to be determined and used separately for every concentration studied.

**B 2; D 4;** Textbooks of Physical Chemistry.

**Activity coefficient.** See Activity.



### Acylation

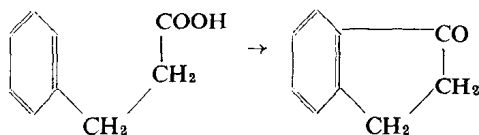
The replacement of a hydrogen atom in an organic compound by an acyl group ( $\text{RCO-}$  or  $\text{ArCO-}$ ).

- (1) Friedel-Crafts acylation (see there).
- (2) Acetoacetic ester (Claisen) condensation (see there).
- (3)  $\beta$ -Diketones can be prepared by the base-catalysed acylation of ketones containing  $\alpha$ -hydrogen atoms, by esters, acid anhydrides or acid chlorides:



The basic catalyst may be Na,  $\text{NaNH}_2$ ,  $\text{RONa}$ ,  $\text{NaH}$ , etc. (OR VIII, 59).

- (4) Kostanecki acylation (see there).
- (5) Intramolecular acylation: ring closure of an aryl-substituted aliphatic acid to form a cyclic ketone, e.g.



This is a special case of the Friedel-Crafts acylation (OR II, 114).

- (6) Acylation of hydroxyl or amino groups can be carried out using organic acids, anhydrides or acid halides (CR 52, 258; see also Schotten-Baumann reaction, Thiele acetylation).

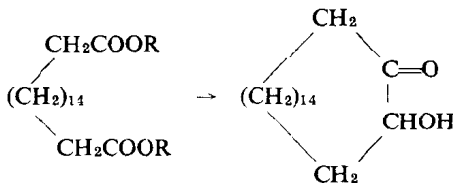
A 1-16; E 1-17.

### Acyloin condensation

- (1) The preparation of an aliphatic  $\alpha$ -hydroxyketone by treatment of an ester with sodium in an inert solvent:



Under carefully controlled reaction conditions, yields are fair to good. Better yields are obtained from the reaction of esters of long-chain dicarboxylic acids, in which case cyclic  $\alpha$ -hydroxyketones are obtained, e.g.



- (2) See Benzoin condensation.

OR IV, 257; A 1-16; B 8, 283.