A LABORATORY MANUAL OF QUALITATIVE ORGANIC ANALYSIS

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PREFACE

This short manual was originally compiled for the use of students attending classes in practical organic chemistry in the University of Manchester. It has been used for several years, first in type-written form, and later in a privately printed edition. It is now published in the hope that others may find it useful.

In writing this book, the author's principal aim has been to present a logical method for the identification of the commoner types of organic compound. The procedure put forward is, in principle, similar to that of Mulliken, in that it consists of a series of tests for functional groups, which are to be applied in a definite order, and it has proved reliable in dealing with substances and mixtures such as are likely to be encountered by the student.

The final step in the identification of an organic compound normally involves the preparation of several crystalline derivatives of characteristic melting-point. In selecting the derivatives to be included in the tables of melting-points, three main considerations have been borne in mind. First, the derivatives should be easy to prepare; secondly, the melting-points of a large number of such derivatives should be known; and thirdly, the necessary reagents should be readily available, and should be suitable for use by students. Where a reaction of a general type, such as nitration, is employed for the preparation of a derivative, different conditions are required according to the particular substance involved. An attempt has been made to group together the numerous variations of method found in the literature into a relatively small number of standard procedures, and to indicate which procedure is to be used for each specific substance.

Discordant values for the melting-points of many substances are recorded in the literature; in compiling the tables contained in this book, the author has tried to select those values which appear to be the most reliable but such selection is inevitably open to error.

It is possible that, in some cases, the discrepancies are due to thermometric errors; where a choice between 'corrected' and 'uncorrected' melting-points is available, the latter have been employed, since the majority of melting-points recorded in the literature are 'uncorrected'. Although experience in the use of these tables has enabled the author to correct a number of mistakes which were originally present, he realizes that other errors may have escaped detection, and he will be glad to be informed of any such errors, either of data or of method, which may be encountered by users of the manual.

Although the information contained in this book is sufficient for the identification of the majority of common substances, the student should be encouraged to seek further information, whenever necessary, in the larger text-books or the original literature.

Whilst it is impossible to make specific acknowledgement of all sources of information to which reference has been made during the compilation of this manual, the author wishes to express a general indebtedness to the authors of other works on the subject, in particular those mentioned on p. 21. He also wishes to express his very sincere thanks to Professor A. R. Todd, F.R.S., for his continued interest and encouragement, and to his colleagues at Manchester, especially Dr F. S. Spring and Dr C. Horrex, for much valuable advice and constructive criticism.

H. T. O.

UNIVERSITY OF MANCHESTER
November 1945

PREFACE TO THE SECOND EDITION

Experience gained in the use of this book since its original publication has brought to light a few errors, omissions and obscurities, and has suggested some improvements. As the need for reprinting has arisen, opportunity has been taken of making suitable alterations and corrections. At the first reprinting, the principal change was the introduction of the hydroxamic test for esters (p. 9). In the present revision, the most important changes are the deletion of the unsatisfactory stannous chloride test for nitro-compounds on p. 14, and the simplification of the alternative and reliable titanous test. Fuller details are included for the recognition of azo-compounds (p. 15), and for the hydrolysis of anilides (p. 75). Few corrections have been found necessary in the tables, but the table of ketones (p. 51) has been considerably altered; elimination of some of the rarer substances has made room for the inclusion of several ketones which have recently become readily available commercially. A number of minor alterations have also been made throughout the book.

The author wishes to thank those who, either by private communication or in reviews, have made suggestions for the improvement of this manual.

H.T.O.

UNIVERSITY OF ST ANDREWS
July 1950

PREFACE TO THE THIRD EDITION

In preparing the third edition of this book, the text has been extensively revised, and partly rewritten, without altering the general character of the book. The most important change involves the treatment of polyfunctional compounds. Instead of concentrating almost entirely on the functional group first detected, the student is now directed to search for other functional groups by applying those further specified tests which are not invalidated by the presence of the principal function.

Other important changes include modified and expanded directions for the detection of constituent elements, and various improvements of procedure in the conduct of the classifying tests (especially the use of potassium bicarbonate instead of sodium bicarbonate in testing for acids). The section dealing with nitrogenous bases (p. 13) has been completely revised to give a more rational treatment. A new section on the investigation of metallic salts has been introduced. New, simplified or improved methods have been given for the preparation of a number of derivatives, and a reliable procedure for the iodoform test has been included.

The tables have also been thoroughly checked and revised, and in some cases considerably expanded. The aim has been to widen the scope of the *Manual*, as far as is practicable, to include all substances available commercially in a reasonably pure condition at a retail price not exceeding £3 per kilogram.

Contrary to the practice in the earlier editions, 'corrected' melting-points have been used in the tables in preference to 'uncorrected', whenever a choice was available. It has been found in practice that, if thermometers calibrated for 3 in. immersion are used in the usual melting-point apparatus, even though they may be immersed to a depth of only 1 in., the stem correction is insignificant and the readings obtained correspond to 'corrected melting-points'.

In order to accommodate the various additions to the text and tables, without appreciably increasing the size of the book, a number of minor deletions have been made from the text, and some less common substances have been omitted from the tables.

H.T.O.

UNIVERSITY OF ST ANDREWS
May 1954

SAFETY NOTE

Some compounds previously included in the tables are now known to be actual or potential carcinogens and have been deleted. Because of the possibility of producing carcinogenic derivatives by nitration, it is recommended that naphthalene, fluorene and diphenyl should not be issued to students as 'unknowns'. It must be emphasized that *all* unknown substances and derivatives should be treated as potentially toxic and handled accordingly. Skin contact and unnecessary inhalation must be avoided.