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**VOGEL'S | ELEMENTARY PRACTICAL
ORGANIC CHEMISTRY 1
PREPARATIONS**

Third edition
Revised by

Dr B. V. Smith

Lecturer in Chemistry, Chelsea College, Lon

Dr N. M. Waldron

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Although many of the spectra quoted are from our own collections and the original literature, we acknowledge the inclusion of spectral information from many other collections. The Aldrich Library of Infrared Spectra, C. J. Pouchert, Aldrich Chemical Co., Milwaukee, Wisconsin; The Aldrich Library of Nuclear Magnetic Resonance Spectra, C. J. Pouchert and J. R. Campbell, Aldrich Chemical Co., Handbook of Chemistry and Physics, 57th Edition, Chemical Rubber Publishing Co., Cleveland, Ohio; H. M. Hershenson, Infrared Absorption Spectra Index for 1945-57, also Ultraviolet and Visible Spectra Index for 1930-1954 and 1955-1959, Academic Press Inc., New York; Sadtler Collections, Standard Infrared Spectra, Standard Ultraviolet Spectra and Standard Nuclear Magnetic Resonance Spectra, Sadtler Research Laboratories, Philadelphia; High Resolution NMR Spectra Catalogues Vols 1 and 2, Varian Associates, Palo Alto, California, USA.

PREFACE

In the twenty one years since this volume was first published it has become well-known for the training of undergraduate practical organic chemists because of the quantity and variety of preparations included and the detailed descriptions of apparatus and technique. In this revision, the range of preparations has been extended and all apparatus and descriptions brought thoroughly up to date so as to provide a sound and valuable basic student text.

The gradual adoption of chromatographic and spectroscopic methods has revolutionised the practice of organic chemistry so that, besides revising and extending the book, some reorganisation of its contents has become necessary. Two new chapters have been created: Chapter III, Essential Laboratory Operations, which is a complete techniques course for the modern organic chemist and Chapter VI, Heterocyclic Compounds has been introduced since very few preparations of this type were to be found in the old edition. Although these chapters contain material from the previous book the majority of each is new. Many new preparations involving novel apparatus, different mechanisms and new reagents have been introduced into the reorganised Aliphatic, Aromatic and Heterocyclic chapters. Because of the redistribution of material in the book the contents of the old Chapter V have been incorporated elsewhere. All the preparations have been rewritten in a different style and spectral measurements have been added to each preparation. To prevent this edition increasing too much in size, pruning has taken place throughout the book, in theory, mechanisms and descriptions of apparatus. Some preparations have been removed to make way for a larger number of new ones.

Chapter I on the Theory of General Technique has been retained though reduced to approximately half its original size. In Chapter II, older glass apparatus has been replaced by equipment with interchangeable ground glass joints and the use of this type of apparatus is assumed in descriptions throughout the book. The opportunity has been taken to reorganise the sections in Chapter II into four logical parts: Individual Items of Equipment, Reaction and Distillation Methods, Solvents and Liquid Extraction Methods, and Melting Point and Crystallisation Methods. All these sections have been revised and include new apparatus. The concept of Chapter III as a 'techniques course' has already been mentioned. It commences with instructions for work in the laboratory, the determination of melting points and boiling points, and recrystallisation to be found in the previous edition. The next part, Methods of Separation, contains new sections on Acid-Neutral and Base-Neutral

Separations, Gas-Liquid Chromatography and Gel Filtration in addition to the other six completely reworked chromatographic sections. The chapter closes with spectroscopic sections designed to assist the student in his understanding of the infrared, ultraviolet and nuclear magnetic resonance spectra which he can record whilst carrying out the preparations in the book. The intention is to give a background for the student in the routine recording of spectra, since it is impossible in the space available to give a full treatment to these techniques.

In Chapter IV, Aliphatic and Alicyclic Compounds, Chapter V, Aromatic Compounds and Chapter VI, Heterocyclic Compounds, the procedures have all been rewritten with the quantities in parentheses following the name of the material to encourage students to write their reports in the style of the Journal of the Chemical Society and to obviate some grammatical difficulties which students encounter. Spectroscopic data has been included with the preparations in a way which we believe has not been attempted elsewhere. We have quoted, in abbreviated form, infrared, ultraviolet and nuclear magnetic resonance spectra of starting materials and products at the end of each preparation in the hope that it will be possible for the student to record these spectra of his own materials and thus check their identity and purity. The preparations may, of course, be followed without the spectroscopic work but we feel that the integration of spectroscopy with the preparative work is desirable and it can only increase in importance in the future. Teachers of the subject may also find the spectra useful for tutorial exercises.

The preparative methods (some of which are well-known named reactions) introduced in this edition are: Simmons-Smith cyclopropanation (IV,3), Wittig reaction (IV,5), Hydroboration (IV,7), Allylic bromination (IV,15), Acyloin synthesis (IV,23), Catalytic hydrogenation (IV,39), Dieckmann cyclisation (IV,40), Enamine alkylation (IV,41), Carbodi-imide peptide synthesis (IV,45), Azlactone reaction (IV,56 and VI,7), Iodination in concentrated sulphuric acid (V,9), Reductive alkylation (V,17), Leuckart reaction (V,20), Optical resolution (V,21), Generation and trapping of benzyne (V,39), Gattermann formylation (V,60), Partial oxidation of an aromatic side chain (V,61), Selective reduction by modified lithium aluminium hydride (V,62), Selective allylic oxidation (V,63), and the following named reactions - Doebner (V,66), Reformatsky (V,88), Knorr (VI,2), Hantzsch (VI,3) and Bischler-Napieralski (VI,15). Directions for the following forty-three compounds are now included and the details given are either applications of well-known methods in the chemical literature or modifications introduced in the light of experience: Norcarane (IV,3), Methylenecyclohexane (IV,5), Hexan-1-ol (IV,6), 2-Phenylethanol (IV,7), 3-Bromocyclohexene (IV,15), Butyrolin (IV,23), 2-Ethoxycarbonylcyclopentanone (IV,40), 2-Ethoxycarbonylcyclohexanone (IV,41), Glucosazone (IV,48), Glycine Ethyl Ester Hydrochloride (IV,52), Glycylglycine Hydrochloride (IV,53), L-Serylglycine (IV,54), N-Phenylglycine (IV,55), DL-Phenylalanine (IV,56), *m*-Iodobenzoic Acid (V,9), *p*-Toluenesulphonic Acid (V,11), *N*-Phenyl-*p*-toluenesulphonamide (V,15), *N*-Benzylaniline (V,17), *N*-Methylaniline (V,18), 1-Phenylethylamine (V,20), *N,N*-Dimethyl-*m*-nitroaniline (and the *p*-isomer) (V,24), Triptycene (V,39), Mesitaldehyde (V,60), *p*-Nitrobenzaldehyde (2 methods - V,61 and V,62), Cinnamaldehyde (V,63), *p*-Methoxycinnamic Acid (V,66), Ethyl 3-Hydroxy-3-phenylpropionate (V,88), 2,5-Dimethylpyrrole (VI,1), 2,4-Diethoxycarbonyl-3,5-dimethylpyrrole (VI,2), 2,6-Dimethyl

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We hope that this revision will increase the scope and usefulness of this book and that the newer approach to preparative exercises will commend it as an undergraduate text. Comments and suggestion from practising teachers will be welcomed by the authors.

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Chelsea College, London
July 1979

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CHAPTER I

THEORY OF
GENERAL TECHNIQUE

THEORY OF DISTILLATION

I,1 VAPOUR PRESSURE If a liquid is admitted into a closed evacuated space, it will evaporate or give off vapour until the latter attains a definite pressure, which depends only upon the temperature. The vapour is then said to be saturated and its pressure at a constant temperature is independent of the quantity of liquid or vapour present. The vapour pressure is usually expressed in terms of the height of the mercury column which will produce an equivalent pressure.

The vapour pressure of a liquid increases with rising temperature. A few typical vapour pressure curves are collected in Fig. I,1. When the vapour pressure becomes equal to the total pressure exerted on the surface of a liquid, the liquid boils. If the vapour can then be constantly removed, as in distillation, then the temperatures of the liquid and vapour do not rise further but, as more heat is supplied, more vapour is formed. **The boiling point** of a liquid may be defined as the temperature at which the vapour pressure of a liquid is equal to the external pressure exerted at any point upon the liquid surface. This external pressure may be exerted by atmospheric air, by other gases, by vapour and air, etc. The boiling point at a pressure of 760 mm of mercury, or 1 standard atmosphere may be termed the **normal boiling point** of a liquid.

The SI unit for pressure is the Pascal (Pa), which is defined as a Newton per square metre (N m^{-2}), but, because of practical simplicity, it is much easier for the organic chemist to measure the pressure in millimetres of mercury (mmHg). If the student should require it the relationship between millimetres of mercury and the Pascal is:

$$1 \text{ mmHg} \approx 133.322 \text{ Pa}$$

It is necessary to know the pressure when a liquid is being distilled, as it will be seen from Fig. I,1, that the boiling point rises with increased pressure and falls with reduced pressure. If no pressure is recorded when a boiling point is given, then it is assumed that the pressure was 760 mm. When, during a distillation, the apparatus is connected to a pump to reduce the pressure, then the boiling point falls. Advantage is taken of the lower boiling point under diminished pressure in the distillation of substances which decompose upon heating to the boiling point under atmospheric pressure; thus ethyl acetoacetate, which boils