# RECENT ADVANCES IN ORGANIC CHEMISTRY

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*ILLUSTRATED*

WITH THE ADDITION OF PART II
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# PREFACE

The present volume contains an account of the developments in some of the newer fields of organic chemistry.

Fresh chapters have been written for this edition on the diterpenes and triterpenes, the problems presented by the decalins and other fused ring-sytems, and the peculiar isomerism of the diphenyl derivatives. Other sections have been revised or rewritten when this seemed necessary. These alterations and additions have added about fifty pages to the size of the volume.

As can be seen from the table of contents, an effort has been made to strike a fair balance in the space allotted respectively to problems of constitution and theoretical questions.

The references to the literature are indicated by figures, whilst footnotes are distinguished by asterisks, etc. In this way the reader will be saved unnecessary glances at the foot of the page.

The book will, it is hoped, serve to guide the reader in the fields with which it deals, and encourage him to go further in the study of the various subjects discussed, since this is the main function of a work of this kind.

In conclusion, I desire to acknowledge the great assistance which has been given to me by Professor D. N. M'Arthur, Dr. H. Graham, and Mr. N. S. Capper, to whom I am indebted for their help in proof reading, and also for suggestions which have led to improvements in the text of the volume.

ALFRED W. STEWART.

The Donald Currie Laboratories,
The Queen's University of Belfast,
*December*, 1930.

# NOTE TO ADDITIONAL CHAPTERS

Some months ago Messrs. Longmans asked me to furnish some fresh material which would bring this volume up-to-date; but at that time I was suffering from eye-trouble which precluded me from undertaking the task.

In these circumstances, Dr. Graham very kindly came to my assistance and consented to write a supplement to the volume, dealing with fresh subjects such as the vitamins, hormones, sterols, etc. The credit and the responsibility for this supplement are his entirely; whilst the limitations of space laid upon him have made his task one of unusual difficulty. I can only record my gratitude to him for making the volume much more interesting than it was.

A. W. STEWART.

The Queen's University of Belfast,
*27th August*, 1935.

# CONTENTS

## CHAPTER I

## ORGANIC CHEMISTRY IN THE TWENTIETH CENTURY

## CHAPTER II

## SOME CARBOHYDRATE CONSTITUTIONS

## CHAPTER III

## THE SESQUITERPENE GROUP

## CHAPTER IV

## THE DITERPENES AND TRITERPENES

## CHAPTER V

## RUBBER

## CHAPTER VIII

## THE CHLOROPHYLL PROBLEM

## CHAPTER IX

## THE DEPSIDES

## CHAPTER X

## SOME THEORIES OF THE NATURAL SYNTHESES OF VITAL PRODUCTS

## CHAPTER VI

## RECENT WORK ON THE ALKALOIDS

## CHAPTER VII

## THE ANTHOCYANINS

## CHAPTER XI

## SOME CASES OF ISOMERISM IN CYCLIC COMPOUNDS

## CHAPTER XII

## THE DIPHENYL PROBLEM

## CHAPTER XIII

## NEW ORGANO-ALKALI COMPOUNDS

## CHAPTER XIV

## OTHER CASES OF ABNORMAL VALENCY

## CHAPTER XV

## CHAPTER XVI

## SOME APPLICATIONS OF ELECTRONICS TO ORGANIC CHEMISTRY

## CHAPTER XVII

# PART II

## CHAPTER XVIII

## THE BILE ACIDS AND STEROLS

## CHAPTER XIX

## THE CARDIAC AGLUCONES (THE VEGETABLE HEART POISONS)

## CHAPTER XX

## THE HORMONES

## CHAPTER XXI

## THE VITAMINS

## PLATES

# RECENT ADVANCES IN ORGANIC CHEMISTRY

## CHAPTER I

### ORGANIC CHEMISTRY IN THE TWENTIETH CENTURY

In the form in which it exists to-day, organic chemistry may be said to take its root in the work of Frankland[1] at the middle of last century. Once the doctrine of the constancy of valency was accepted, the way was open for Couper[2] and Kekulé[3] to bring order into the vast mass of material which had been accumulated in earlier times; while, later, van't Hoff[4] and Le Bel[5] carried the ideas of molecular arrangement out of two dimensions into three and laid the foundation of our present views. Following in the track of these pioneers, the chemists of the latter half of the nineteenth century rapidly developed the theoretical side of the subject; while, on the other hand, the modern formulæ lent to synthetical work a certainty which had previously been unknown.

Despite the Briarean efforts of the synthetic school, it is safe to say that the latter half of the nineteenth century will be regarded as a time when theoretical speculation played the main part in the development of the subject. Of the hundred thousand organic compounds prepared during that time, the majority were still-born and their epitaphs are inscribed in

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[1] Frankland, *Phil. Trans.*, 1852, **142**, 417.

[2] Couper, *Phil. Mag.*, 1858, iv., **16**, 104.

[3] Kekulé, *Annalen*, 1866, **137**, 129.

[4] van't Hoff, *Voorstell tot uitbreiding der structuur formules in de ruimte* (1874).

[5] Le Bel, *Bull. Soc. chim.*, 1874, ii., **22**, 377.

Beilstein's Handbook. Compared with the great clarifying process which laid the basis of our modern views, they weigh but little in the balance.

The new century opened under different auspices. At first it seemed as though the discoveries in electronic physics would have their reaction upon our structural views; but though several attempts[1] have been made in this region of the subject, organic chemists in general have not welcomed them with anything like whole-hearted encouragement. There is a feeling, apparently, that in abandoning the usual structural formulæ and replacing them by electronic symbols the subject is being complicated instead of simplified; and this feeling, whether it be due to scientific caution or to mere conservatism, has certainly carried the day for the present.

During the last fifty years the flood of synthetic material, principally from the German laboratories, has tended to obscure the genesis of what we still, out of respect for tradition, term organic chemistry. In its early days the science was devoted to the study of compounds produced by natural methods in plants and animals; and it is interesting to find that during the new century a return has been made to the older field.

The twentieth century was hardly begun, when in 1903 Komppa devised a synthesis of camphor, and thus cleared up a problem which had engaged the attention of many investigators. Later came the work of Perkin and his school in the terpene group, which gave a fresh impetus to study in this branch of the subject.

In the alkaloid series great strides have been made, both in determining constitutions and in devising synthetic methods of preparing the natural substances; whilst the examination of plants and the extraction from them of new alkaloids is proceeding apace.

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[1] Nelson and Falk, *School of Mines Quarterly*, 1909, **30**, 179 ; *J. Amer. Chem. Soc.*, 1915, **37**, 274 ; Nelson, Beans, and Falk, *ibid.*, 1913, **35**, 1810 ; Falk and Nelson, *ibid.*, 1910, **32**, 1637 ; 1911, **33**, 1140 ; Falk, *ibid.*, 1912, **34**, 1041 ; Noyes, *ibid.*, 1912, **34**, 663 ; Fry, *ibid.*, 1912, **34**, 664 ; 1914, **36**, 248, 262, 1035 ; 1915, **37**, 885 ; 1916, **38**, 1323, 1327, 1333 ; *Zeitsch. physikal. Chem.*, 1911, **76**, 385, 398, 591 ; 1912, **80**, 29 ; 1913, **82**, 665 ; 1915, **90**, 458 ; Stark, *Jahrb. Radioaktiv Electronik*, 1908, **5**, 124 ; 1909, **6**, 12 ; 1912, **9**, 15 ; *Physikal. Zeitsch.*, 1912, **13**, 585 ; G. N. Lewis, *Valence* (1923).

In the carbohydrate group the problem which looms behind most of the modern investigations is the constitution of the celluloses. The celluloses have extremely complicated structures; and it was only by breaking up their molecules into simpler compounds and then identifying these that we could hope to determine the constitution of the parent substance. The first step in this direction was evidently to obtain and identify readily purifiable carbohydrate derivatives such as methyl ethers, acetyl derivatives, etc. Then by methylating or acetylating celluloses themselves previous to breaking them up, it is possible to recognize among the decomposition products certain well-defined fragments which permit of guesses being made at the structure of the original molecule. This method in the hands of Purdie, Irvine and their collaborators * has already given us the key to the constitution of cotton cellulose; and now that the road has been opened, it is not unreasonable to expect a rapid increase in our knowledge of this field.

Much more complicated is the riddle of the protein molecules. Although there is a surface similarity between proteins and celluloses owing to the fact that both molecular types are liable to fission under the action of hydrolysing agents, the decomposition products of the proteins are far more complex than those resulting from the break-down of celluloses. Fischer's work on the polypeptides has been a first step towards a more exact knowledge of the protein constitutions; but it is a very short step on a very long road.

The methods devised by Fischer in his investigation of the polypeptides served him later in his researches on the tannins.† In 1912, he put forward the view that the natural tannins were fully esterified glucoses in which digalloyl nuclei replaced the hydrogen atoms of hydroxyl groups; and this conception of the tannin structure was justified by his synthesis of penta-(*m*-digalloyl)-$\beta$-glucose, which closely resembles Chinese tannin in its properties. It must not be too hastily assumed, however, that Fischer's researches have furnished a key to the structure of all classes of tannins.

Turning to natural pigments, it will be found that the present century has seen a great advance in our knowledge. Kostanecki's researches on the flavone derivatives established the

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* See Chapter II.

† See Chapter IX.

constitutions of many of the natural dyes. Willstätter's work on chlorophyll * has given us some insight into the nature of that mysterious substance, though it would be going too far to claim that even yet we know much about the chlorophyll structure; whilst in the field of flower pigments the same investigator has established the general character of the anthocyanins † and has practically reduced future work to a stereotyped line.

The examination of the colouring matters of the blood and of the bile has opened up yet another branch of pure "organic chemistry"; and the parallelism established between hæmin and chlorophyll suggests most interesting reflections as to the origin of these two natural substances which play so great a part in animal and vegetable economy.

So much for the effects of a return to the original aims of organic chemistry. When the purely synthetic side of the subject is examined, it must be admitted that, with some notable exceptions, the results are of much less general interest. Of new compounds there is no lack, certainly; but there is a distinct dearth of interesting materials. One or two examples may be given here of substances which have an interest for chemists other than the mere specialist.

The discovery of the ketens by Staudinger brought to light a completely fresh class of substances of remarkable reactivity; and the problem of the relative activities of the carbonyl and ethylenic bonds in these compounds promises eventually to throw light upon some aspects of chemical linkages. Work in the field of the ketens has also clarified our ideas with regard to the nature of the aliphatic diazene derivatives.

By far the most interesting set of compounds prepared in the last quarter of a century has been the derivatives of various elements in a state of abnormal valency. Gomberg's triphenylmethyl seemed at first likely to remain without a parallel; but in recent times a perfect flood of abnormalities has been let loose by further investigation. The aryl derivatives of the alkali metals, the metal-ketyls,‡ the tri-aryl-methyl series, to name only a few, have forced upon the notice of chemists the fact that the old and apparently well-tried dogma of the permanent quadrivalence of carbon is in a very shaky condition. By the researches

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* See Chapter VIII.

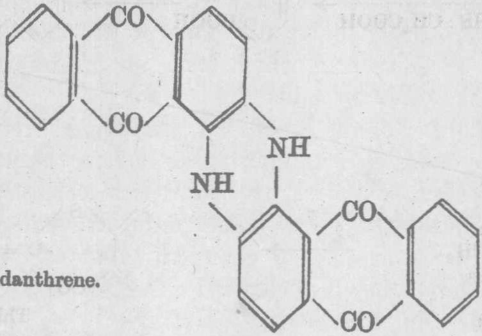
† See Chapter VII.

‡ See Chapter XIII.

in these and allied fields,* carbon has been definitely ranked among the ionogenic elements; and the way was made open for the ready acceptance of G. N. Lewis's general theory of valency on the electronic basis.

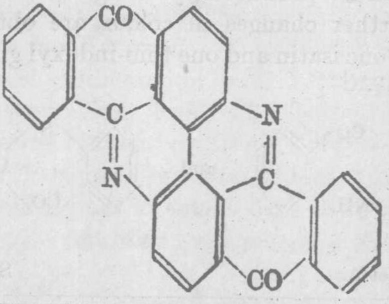
On the technical side organic chemists have not been idle. The great dye industry pours out its flood of colour; and although as a general rule its products have a commercial rather than a scientific interest, two classes deserve notice here.

Vat dyes are those which, like indigo, are almost insoluble in water, but yield on reduction leuco-compounds soluble in alkali. The actual dyeing process is carried out by impregnating the fabric with the leuco-compound and then allowing or forcing oxidation to take place. The earliest example of the anthraquinone vat dyes, indanthrene, was produced in 1901. It is prepared by fusing 2-amino-anthraquinone with alkali, or by condensing 1-amino-anthraquinone with itself :—



Indanthrene.

To the same class belongs flavanthrene :—



Flavanthrene

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* See Chapter XIV.