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Carbohydrate Chemistry

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during 1976

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Organic formulae composed by Wright's Symbolset method

Preface

This Report, the tenth in the series, covers the literature available to us between mid-January 1976 and mid-January 1977. With the publication of this volume, the number of Reports in the series has reached double figures: we hope that this Report maintains the standards set by its predecessors in summarizing the recent literature in carbohydrate chemistry in a concise, lively, and palatable form. Once again the literature coverage is comprehensive, rather than selective, although inevitably a few papers are missed each year—we are grateful when these are brought to our attention for inclusion in a subsequent Report.

As has been our policy in previous years, *Abstracts of the American Chemical Society Meeting* and the patent literature have not been abstracted. The abbreviation 'Bn' is again used throughout to denote the benzyl group.

Dr. J. M. Williams has joined our team of Reporters for Part I.

We thank Dr. L. C. N. Tucker for reading and commenting on the whole of Part I, and Mrs. Alice Duncan, Miss Moira Endersby, and Miss Lynda Esplin for typing almost all of this Report.

Finally, it is a pleasure to acknowledge the invaluable assistance provided by Philip Gardam and his staff at the Chemical Society in the production of this Report.

August 1977

J. S. B.

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Abbreviations

The following abbreviations have been used:

ADP	adenosine diphosphate
ATP	adenosine triphosphate
c.d.	circular dichroism
CDP	cytidine diphosphate
CMP	cytidine monophosphate
DBU	1,5-diazobicyclo[5,4,0]undec-5-ene
DCC	dicyclohexylcarbodi-imide
DEAE	diethylaminoethyl
DMF	<i>NN</i> -dimethylformamide
DMSO	dimethyl sulphoxide
DNA	deoxyribonucleic acid
dpm	dipivaloylmethanato
e.s.r.	electron spin resonance
fod	2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato
g.l.c.	gas-liquid chromatography
HMPT	hexamethylphosphortriamide
i.r.	infrared
NBS	<i>N</i> -bromosuccinimide
n.m.r.	nuclear magnetic resonance
o.r.d.	optical rotatory dispersion
py	pyridine
RNA	ribonucleic acid
THF	tetrahydrofuran
Thp	tetrahydropyranyl
TMS	trimethylsilyl
UDP	uridine diphosphate

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Introduction

Part I

MONO-, DI-, AND TRI-SACCHARIDES AND THEIR DERIVATIVES

By

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1 Introduction

The general terms of reference remain those set out in the Introduction to Volume 1 (p. 3) and the arrangement of subject matter follows that of previous Reports in this Series.

New methods, including the use of trifluoromethanesulphonic anhydride, have been reported for activating the anomeric centre of sugars for the synthesis of glycosides and higher saccharides, and trialkylstannylation has been found to enhance the nucleophilicity of the hydroxy-groups of simple and complex aglycones in the formation of glycosides from acetylated glycosyl halides (Chapter 3). A new method for the synthesis of 1,2-*trans* alkyl glycosides, which circumvents the use of glycosyl halides, has involved the reaction of peracylated sugars with a DMF dialkyl acetal in the presence of a Lewis acid catalyst (Chapter 3).

Among other interesting developments to be reported during the past year are the use of phase-transfer catalysts in the preparation of fully or partially alkylated sugar derivatives (Chapter 4) and of 2,3-*O*-dibutylstannylene derivatives in the selective esterification of HO-2 of certain methyl α -D-hexopyranosides, without the need to protect the primary hydroxy-group (Chapter 6). Moreover, alkylation of *cis*-2,3- or -3,4-*O*-dibutylstannylene pyranosides has been shown to occur regioselectively at the equatorial oxygen atom (Chapter 18). The knowledge that hydrogenolytic cleavage of the dioxolan ring of alkyl 2,3- and 3,4-*O*-benzylidenepyranosides depends on the configuration of the acetal carbon atom has also opened the way to a number of synthetically useful benzyl ether derivatives (Chapter 5). A new procedure for the synthesis of deoxy-sugars has involved the opening of diol thiocarbonates in a radical fashion with tributyltin hydride (Chapter 13).

Many and varied syntheses of aminoglycoside and nucleoside antibiotics and their analogues are reported in Chapters 20 and 21. Careful labelling studies over the past year or so, particularly by Rinehart's group, have provided information on the biosynthetic pathways that convert D-glucose into the aminocyclitol moieties of streptomycin and spectinomycin (Chapter 20).

Another report has shown the need to use ^{13}C -labels in making unambiguous assignments to resonances in the ^{13}C n.m.r. spectra of carbohydrates (Chapter 20). Earlier assignments to some of the resonances in the natural abundance ^{13}C n.m.r. spectra of several common monosaccharides have had to be revised in the light of coupling data obtained from the spectra of [1- ^{13}C]monosaccharides, and it is clear that empirical chemical-shift rules for the effects of derivatization must be carefully reassessed. Differences observed between the proton