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SOME ASPECTS OF N.M.R. SPECTROSCOPY AND OF
REARRANGEMENT MECHANISMS

A Thesis
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TABLE OF CONTENTS

ABSTRACT

Part 1. Some Aspects of N.M.R. Spectroscopy	iv
Part 2. Acid-catalysed Rearrangements in Cyclic Systems	vi
Part 3. The Clemmensen Reduction of 1,3-Diketones	vii
Part 4. Intramolecular Hydrogen Abstraction Reactions on Aromatic Alkyl Groups	viii

PART 1

SOME ASPECTS OF N.M.R. SPECTROSCOPY

INTRODUCTION

Long Range Coupling	2
Solvent Effects	21
Hydroxymethylene Ketones	30

DISCUSSION

Long Range Coupling	36
Solvent Effects	50
Hydroxymethylene Ketones	62

TABLE 1	70
TABLE 2	77
TABLE 3	82
TABLE 4	83
TABLE 5, TABLE 6	84
TABLE 7, TABLE 8	85
TABLE 9	86
TABLE 10	88

TABLE 11	90
TABLE 12	91
TABLE 13	93
GENERAL EXPERIMENTAL DETAILS	95
EXPERIMENTAL	96
FIGURE 1, FIGURE 2	117
FIGURE 3, FIGURE 4	118
FIGURE 5	119
FIGURE 6	120
DIAGRAMS	121
REFERENCES	123

PART 2

ACID CATALYSED REARRANGEMENTS IN CYCLIC SYSTEMS

INTRODUCTION	133
DISCUSSION	
Rearrangements of cross-conjugated methylenecyclohexadienes	144
Rearrangements of α 'Hydroxycyclohexenones	150
TABLE 1	165
EXPERIMENTAL	
Rearrangements of cross-conjugated methylenecyclohexadienes	166
Rearrangements of α 'Hydroxycyclohexenones	185
DIAGRAMS	221
REFERENCES	229

PART 3THE CLEMMENSEN REDUCTION OF 1,3-DIKETONES

INTRODUCTION	238
DISCUSSION	249
EXPERIMENTAL	263
REACTION SCHEMES	275
DIAGRAMS	284
REFERENCES	286

PART 4INTRAMOLECULAR HYDROGEN ABSTRACTION REACTIONS ON
AROMATIC ALKYL GROUPS

INTRODUCTION	291
DISCUSSION	298
EXPERIMENTAL	304
DIAGRAMS	321
REFERENCES	325
ACKNOWLEDGEMENTS	328

ABSTRACTPART 1SOME ASPECTS OF N.M.R. SPECTROSCOPY

A review of coupling mechanisms is given and notable examples of long range coupling in the literature are discussed. Methyl protons can undergo long range coupling with protons which are 4 σ bonds away, and the mechanism of this process as related to the known examples is discussed. Application of the phenomenon in solving stereochemical problems is also discussed. The effects of electronegative substituents on long range coupling is also outlined.

A Discussion of the present work follows, wherein the description of the preparation of many bornane derivatives, including several deuterated derivatives, is presented. The line widths ($W_{h/2}$) of the methyl groups were measured. It was found that the width of the methyl groups decreased in the order $C_8 > C_9 > C_{10}$, and the C_8 and C_9 methyl signals were always appreciably broader than the C_{10} . Long range coupling between the protons of the C_8 and C_9 methyl groups is postulated as being responsible for these two being broader than C_{10} . Long range coupling between the C_8 methyl protons and the C_5 and C_6 endo protons, and between the C_9 methyl and the C_3 endo proton is tentatively ascribed to the differences in the widths of the C_8 and C_9 methyl groups.

Although the line widths of the tertiary methyls were found to

vary with solvent, the relative widths of the three methyl signals of the bornane derivatives was found to be the same. Thus measurement of line widths is a method of correlating the methyl signals in spectra run in different solvents.

The effects on the chemical shifts of the tertiary methyl groups of bornanes when various substituents are placed in the basic skeleton, is also described. The presence of an ethylenedioxy group at C₂ or C₃ results in a deshielding of C₈ and a shielding of C₉, while introduction of hydroxyl groups has no uniform effect because of different orientations of the hydroxyl group from compound to compound.

An introduction to the mechanism of benzene induced solvent shifts is given. Benzene appears to form a stereospecific complex with ketones, and other molecules, which can undergo a dipole - induced dipole interaction. The effects of this interaction on the n.m.r. spectra of various ketones, quinones and aromatic compounds is described.

The present work describes the measurement of solvent shifts at various concentrations of ketones and ketals in benzene. Previous similar work is discussed in the light of the results obtained, and it has been shown that some assumptions previously used in correlating the data with the interactions, have been unjustified. The solvent shifts versus the concentration have been plotted to give curves which have been interpreted as indicating specific solvent - solute interactions, i.e. 1 : 1, 1 : 2, etc., and not random associations. This has been shown by comparing calculated curves with the experimental results, with which agreement is good.

The third part of this section of the work deals with the spectra of some hydroxymethylene ketones, and commences with an introduction to the general behaviour of 1,3-diketones in solution. The rates of exchange of enolizable protons is discussed, and their use in determining the relative proportions of enol forms is outlined.

The present work describes the behaviour of 3-formylbornan-2-one in carbontetrachloride - D₂O solution, and an explanation for the preference for one enol form is given. Also discussed is the coupling between 'formyl' and hydroxyl protons in hydroxymethylene ketones, and it is shown that the coupling depends strongly on the H-O-C-H angle, which can be altered by slight changes in molecular geometry, thus leading to changes in coupling constants. No change in coupling constants caused by temperature differences was observed, and it is speculated that exchange processes do not affect the value of the coupling constant, but only whether coupling occurs.

PART 2

ACID CATALYSED REARRANGEMENTS IN CYCLIC SYSTEMS

A comprehensive review of the dienone - phenol rearrangement is given and it is shown that any cross-conjugated cyclohexadienone will rearrange to an aromatic product, the substitution of which depends strongly on (i) the substitution pattern of the original dienone, (ii) peculiarities in the molecular structure, and (iii) the rearrangement conditions. Rearrangements of some dienols and some cross-conjugated methylenecyclohexadienes or 'semibenzenes' are described, and in general

these follow the pattern of the dienone - phenol rearrangement. Rearrangement of some steroidal α -substituted ketones is also mentioned briefly.

Two cross-conjugated methylenecyclohexadienes were synthesised by reaction of methylmagnesium iodide on the corresponding dienones - this reaction had previously been reported to give only the products of rearrangement of the intermediate semibenzenes. The semibenzenes were rearranged using perchloric acid in acetic anhydride - ethyl acetate to give the 1,4-disubstituted aromatic product. The attacking species was shown to be a proton, and the reaction, unlike the dienone - phenol rearrangement, showed a clear preference for methylene rather than methyl migration.

Several methyl substituted steroidal 2 α -hydroxy-4-en-3-ones were prepared by the rearrangement of the corresponding 4,5-epoxy-3-ones with sulphuric acid in aqueous acetone, herein shown to be a general method. The hydroxyenones were rearranged using three sets of conditions: Toluene-*p*-sulphonic acid in methanol, toluene-*p*-sulphonic acid in benzene, and perchloric acid in acetic anhydride - ethyl acetate. Only one compound, 2 α -hydroxycholest-4-en-3-one gave an aromatic product; the other substrates underwent rearrangement through the various enols, to give attack usually at C₆ of the carbon skeleton. A mechanism is given and discussed for each rearrangement. No general pattern seemed to emerge.

PART 3

THE CLEMMENSEN REDUCTION OF 1,3-DIKETONES

A review of the mechanism of the Clemmensen reduction is given with specific reference to reduction of difunctional compounds, where

rearrangements may occur.

The present work shows that in the Clemmensen reduction of 1,3-diketones, the intermediate cyclopropanediol which is first formed, undergoes acidolysis to give an α -hydroxy ketone and a β -hydroxy ketone, each of which may then undergo further Clemmensen reduction to give the observed rearranged and unrearranged monoketones. The intermediacy of a β -hydroxy ketone was proved by observing the rate of formation of the products, and by measuring the rate of reduction of an independently synthesised α -hydroxy ketone.

Reduction of two acylcyclic ketones was shown to give a ring expanded product only in the case of 2-acetylcyclopentanone.

PART 4

INTRAMOLECULAR HYDROGEN ABSTRACTION REACTIONS FROM AROMATIC ALKYL GROUPS

A short resumé of intramolecular hydrogen abstraction reactions using lead tetraacetate or the hypoiodite process is given, with some detail being applied to the conditions, and the stereochemistry needed for the reaction, and to fragmentation processes which may occur. Brief mention is also made of the new reaction; hydrogen abstraction using decomposition of a hypobromite with silver ions.

The lead tetraacetate reaction was applied without success to abstraction of hydrogen from an aromatic methyl group, utilizing an α -benzylic hydroxyl group. Fragmentation reactions were generally obtained. Application of the bromine - silver ion method gave good yields of cyclic ethers in two cases, indicating that an abstraction reaction had

taken place. The conditions for such a reaction seem to be critical: A tertiary hydroxyl group is required, and the abstraction seems only to take place from a primary centre.