

PREFACE

Andrew Pelter

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

Professor H.C. Brown is one of the scientific giants of our age, a fact long recognised in the numerous awards made to him by his fellow chemists¹ and by the award to him of the Nobel Prize for Chemistry in 1980.

Herb Brown was born in London, U.K. on May 22nd, 1912 and was seeking a living and an education in the Chicago of the 1930's. After overcoming many difficulties² he completed the requirements for the B.Sc. (Chicago) in 1936. Inspired by a gift from Sarah Baylen, his fellow student and now wife of over forty years, of Alfred Stock's 'Hydrides of Boron and Silicon' he joined J.I. Schlesinger in the study of the reduction of carbonyl compounds by diborane, then a chemical curiosity. After obtaining his Ph.D. in 1938 he spent a fruitful year with M.S. Kharasch studying radical reactions. Hence at a very early stage in his career the foundations were laid for his two life long interests, one being the chemistry of derivatives of boron and the other being mechanistic organic chemistry.

In 1939 he rejoined Schlesinger and under the exigencies of the early war years developed methods for the production of the metal borohydrides and some of their derivatives, and studied their chemistry. One of the consequences of this work was that solutions of diborane became readily available. The work was finally published in a classic series of eleven papers in the Journal of the American Chemical Society in 1953, and had a deep and continuing impact on all aspects of chemistry. A glance at 'NaBH₄' in 'Chem. Abstracts' over the last 15 years will emphasise the influence of this early work. At this time LiAlH₄ had been accepted by organic chemists as a powerful reducing agent, and Herb Brown incepted a programme with the objective of making available a series of nucleophilic reducing agents of high selectivity and of reducing power between that of LiAlH₄ and NaBH₄.³ In fact the range has been extended so that the organic chemist can choose reductants, such as 'superhydride' (NaBEt₃H) which are even more powerful than LiAlH₄. At the same time electrophilic reductants such as complexes of borane and alane were being studied, culminating in the report in 1956⁴ of hydroboration as a mild and

and efficient method for the conversion of alkenes to organoboranes in a regio- and stereospecific manner. A far seeing and painstaking exploration of hydroboration followed which, though somewhat underestimated at the time, laid a firm foundation for the explosive expansion of organoborane chemistry that began some ten years later. In over 150 papers on organoboranes, Herb Brown and his colleagues have shown that organoboranes can be intermediates in the formation of C-H, C-O, C-N, C-Hal, C-Metal and above all C-C bonds in a wide variety of contexts.⁵ The introduction of such reactions as the carbonylation of organoboranes has significantly altered the whole concept of organic synthesis and it is true to say that there is no modern major synthesis which does not use either a reagent or a reaction devised by H.C. Brown. A truly massive achievement.

The potentiation of steric and electronic effects in the mechanism of any reaction is a source of continuing interest and importance to organic chemists. At a time when, under the influence of C.K. Ingold and G.W. Wheland electronic effects alone were held to be sufficient to explain the course of organic reactions, H.C. Brown initiated careful and quantitative studies into steric effects.³ He showed that such effects had to be taken account of and introduced the concepts of F, B and I-strains to explain his data. This led on to the introduction of σ^+ constants, originally for substituents in aromatic substitution reactions but later found to be of wider applicability. He also enunciated the Selectivity Relationship, simply summarised as an inverse relationship between selectivity and reactivity.

It was his interest in steric effects that led Herb Brown into questioning the ease with which, in the 1950's and early 1960's, carbonium ions were being assigned 'non classical' (e.g. 2-electron, 3-centre) structures. He pointed out that even when evidence had been adduced, particularly in the case of the norbornyl cation, it was far from unequivocal and that steric effects of potential importance were being overlooked. In a magnificent series of studies he carefully examined the basis for the belief in the non classical nature of the norbornyl cation, showing each one in turn to be questionable. The discussion fascinated the chemical world and is summarised in the book 'The Non Classical Ion Problem' (Plenum Press, New York 1977) in which Herb Brown states his position but, with characteristic fairness allows one of the leading proponents of the other viewpoint to comment chapter by chapter.

The effect of the Herb Brown's studies on the mechanisms of organic reactions has been as deep and wide ranging as his contributions to organic synthesis. Both interests continue to be pursued as actively as ever, to the great benefit of us all.

I finish by considering Herb Brown in a human rather than simply a chemical context. It is impossible to overestimate the effect that a loving and life-long partnership with his wife Sarah has had upon him and on his associates, who form a kind of extended family. Herb Brown has had over 200 younger research associates and colleagues and he and Sarah seem to know the fates and whereabouts of almost all of them and to be ready to extend help, whenever and wherever it is needed. More than fifty of his former students are Members of Faculty and it is good to know that his clear thought and humanity are being transmitted to his 'chemical grandchildren' not only in the U.S.A. Such influence can only be for the good.

Herb Brown is an example to us all, both as a scientist and a human being. We hope to benefit from that example for a long time yet.

References

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