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FOREWORD

Ring forming reactions have for a long time featured prominently in the synthetic arsenal of the organic chemist. The degree of control over relative stereochemistry, coupled with the simultaneous (or nearly so) formation of two bonds and construction of a ring lie at the heart of the utility of this wide range of reactions which have few, if any, natural counterparts. Latterly the realisation has dawned that the high degree of diastereocontrol inherent with cycloaddition reactions makes them ideal candidates for enantioselective synthesis.

The Diels–Alder reaction, with its highly ordered transition state conferring strong regioselectivity and *endo*–stereoselectivity has been the prime candidate for studies relating to asymmetric synthesis This is reflected in the high proportion of the contributions to this Special Issue on *Enantioselective Cycloadditions* which report investigations into Diels–Alder reactions (no fewer than twelve of the papers are concerned with this class of reaction) and bears testament to the high degree of interest that this reaction continues to excite some 63 years after it was first described. Nonetheless, this general framework of '4 + 2 cycloadditions' encompasses wide ranges of dienes and dienophiles, different means for engendering the desired enantio– and diastereocontrol and ingenious synthetic applications. Dienophiles vary from the 2–sulfinylmaleates reported by Carretero, through nitroso derivatives (Streith and Ghosez), to chiral captodative α,β–unsaturated oxazolines (Langlois), imines (Waldmann) and 2(*5H*)–furanones (Feringa). Craig describes an intramolecular variant of the Diels–Alder with sulphoximine substituted trienes and studies involving azadienes are detailed by Bailey. Kabalka and Pagni discuss the effect of alumina catalysis upon diastereoselectivity of Diels–Alder reactions and synthetic applications of this powerful reaction are reported by Cativiela, Narasaka and Fuji.

Of late, much attention has been turned to the possibility of enantiocontrol in 3 + 2 cycloadditions for the generation of 5–membered heterocycles. Azomethine ylids feature in papers submitted by Cinquini and Cozzi, Husson and my own group at Oxford. Nitrile oxides are the subject of a contribution from Kanemasa; while Kim describes work into the reactions of nitronates with chiral dipolarophiles. Brandi presents details of the use of chiral nitrone dipoles and the kinetics of their reactions with chiral vinyl phospholes. Chiral vinyl sulfoxide dipolarophiles form the basis of studies described by Koizumi and Shiro.

The 2 + 2 cycloaddition reaction has not been ignored within the context of enantioselectivity. Font reports studies of diastereoselective photocycloadditions using chiral 2(*5H*)–furanones and Ghosez has contributed a paper describing an elegant application of the intramolecular.2 + 2 cycloaddition of keteniminium salts to the synthesis of prostaglandin precursors. This Special Edition also includes a contribution by Mikami describing studies on the carbonyl ene reaction; the only paper to be concerned with the application of chiral catalysts.

Much has been achieved in pursuit of the 'Holy Grail' of predictable and efficient enantiocontrol of cycloaddition reactions, but much yet remains. The development of working models to provide definitive understanding and rationalisation of the comparative effectiveness of various auxiliaries under specific situations remains our goal. We find herein contributions from Thornton and from Scharf which address these issues in the Diels–Alder and Paterno–Büchi reactions respectively. It is certain that the empirical practical approach to this area will increasingly dovetail with theoretical studies in providing general answers to particular problems.

An issue of necessarily limited size cannot possibly hope to do justice to all the areas of research currently being undertaken in the quest for enantiocontrol of cycloaddition reactions. Nevertheless it is hoped that this Special Issue will present itself to readers as a landmark which encapsulates a cross section of the present range of research effort and current level of achievement in this challenging area of Organic Chemistry. The next few years promise to be an exciting time.

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